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A Cu(I) cluster bearing a bridging phosphane ligand

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ABSTRACT

The solid state structure of a Cu(I) cluster bearing bridging phosphane ligands is described. This Cu₄ cluster results from a formal Cl-abstraction of the CH₂Cl₂ solvent. This derivative is the first example of a multinuclear Cu(I) complex bearing bridging phosphane ligands in which the Cu(I) centers have different coordination geometries. The four Cu(I) ions participate in metallophilic interactions within this cluster. Interestingly, despite the gross molecular structure being highly dissymmetrical, the μ-P atoms bridge symmetrically the metal centers.

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R É S U M É

La structure cristalline à l'état solide d'un cluster de Cu(I) présentant des ligands phosphine pontants est décrite. Ce cluster Cu₄ résulte formellement de l'arrachement d'ions chlorure du CH₂Cl₂ utilisé comme solvant. Ce dérivé est le premier exemple d'un complexe multinucléaire de Cu(I) présentant des ligands phosphine pontants dans lequel les centres Cu(I) pontés ont des géométries différentes. Les quatre ions Cu(I) sont impliqués dans des interactions metallophiles au sein de ce cluster. D'une manière remarquable, en dépit d'une structure moléculaire globale hautement dissymétrique, les atomes μ-P pontent de manière symétrique les centres métalliques.

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1. Introduction

In 2000, Werner et al. reported a new coordination mode for phosphane ligands with the synthesis of the bimetallic Rh(I) complexes **A** (Fig. 1) in which tertiary R₃P derivatives act as bridging ligands [1]. The phosphane ligands are among the most widely used 2-electron donors in coordination chemistry and, prior to Werner's work, they were almost exclusively known as terminal ligands [2]. This seminal discovery was a breakthrough in coordination chemistry, since binucleating ligands potentially allow the synthesis of di- and polynuclear complexes that are of great interest in manifold fields such as

catalysis, bio-inorganic and materials sciences [3]. The second family of stable dimers bearing a bridging phosphane moiety was prepared using the 2,5-bis(2-pyridyl)-phosphole ligand **B** (Fig. 1). In 2001, the Pd^I-dimer **C**₁ having two identical Pd-P bond lengths was isolated (Fig. 1) [4]. Following this observation, mixed Pd^I,Pt^I-complex **C**₂ [5], Cu^I-dimers such as **D**₁₋₃ [5,6] and Ag^I-dimers such as **E**₁₋₂ [7] featuring bridging phosphole moieties were also prepared (Fig. 1). More recently, it has been shown that phenylbis(pyrid-2-ylmethyl)phosphane ligand can also stabilize Cu(I)- and Ag(I)-bimetallic complexes such as **F** (Fig. 1) in which the P-atom acts as a bridging P-center [8].

Dimers assembled by the N,P,N-pincer **B** have found useful utilisation as building blocks in coordination driven supramolecular synthesis; this is an appealing alternative to classic synthetic methodologies for constructing complex molecules. Cu^I-complex **D**₃ and Ag^I-complex **E**₁ can be

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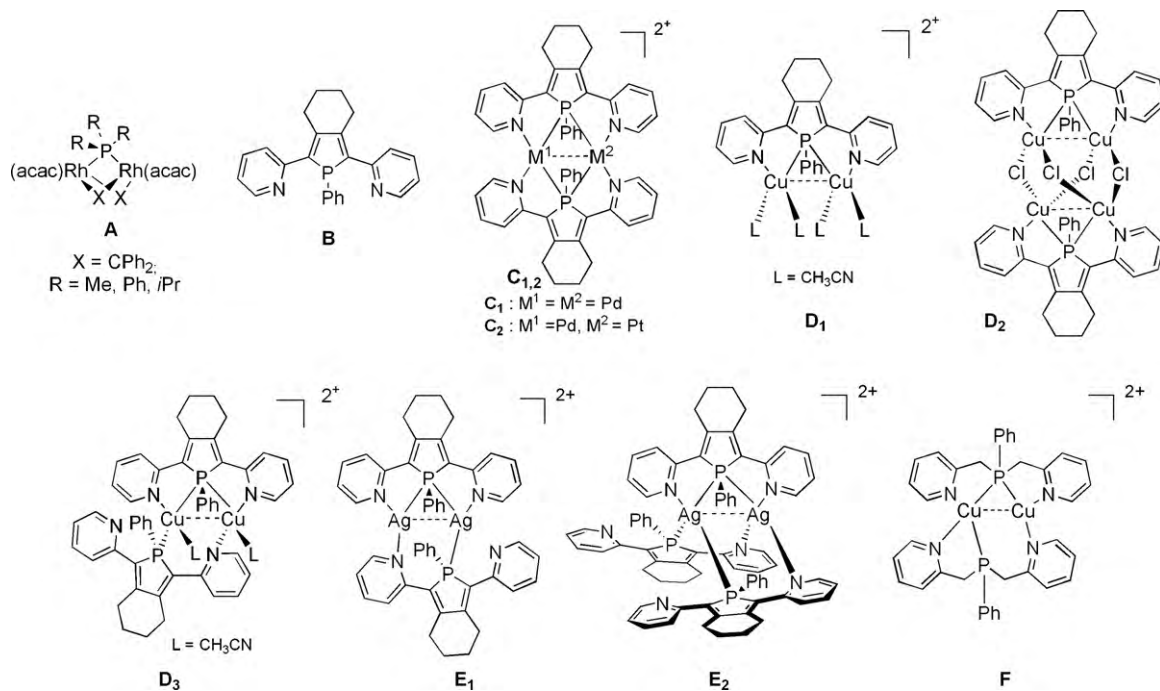


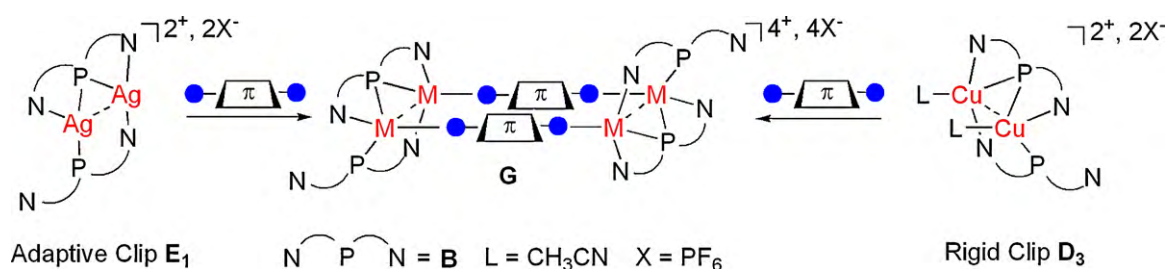
Fig. 1. Chemical structure of ligand **B** and representative examples of metal complexes bearing μ -P atoms.

used as 'rigid' or 'adaptive' bimetallic molecular clips, respectively, for the synthesis of π -stacked metallacycles **G** upon reaction with linear homoditopic linear π -conjugated linkers (Scheme 1) [9,10]. Numerous supramolecular metallacycles **G** based on clips bearing a bridging phosphane ligand have been prepared [9,10] demonstrating that this coordination mode is not 'exotic' since it allows one to stabilize appealing bimetallic building blocks in supramolecular synthesis.

Herein, we report the synthesis and structural characterization of a novel Cu(I) cluster stabilized by the bis(2-pyridyl)phosphole **B** in which the P-center acts as a bridging ligand. This $[\text{Cu}_4\text{Cl}_3]$ complex is obtained via an unusual route since its $[\text{Cu}_4\text{Cl}_3]$ core results from Cl-abstraction from the CH_2Cl_2 solvent. Moreover, this monocationic derivative, that was characterized in the solid state only due to its isolation in low yield, exhibits an original structure with the μ^2 -P centres bridging two Cu(I) centres having different coordination numbers and geometries.

2. Characterization of a monocationic $[\text{Cu}_4\text{Cl}_3]$ cluster stabilized by two ligands **B** bearing a bridging phosphane center

A yellow dichloromethane solution of the Cu(I) dimer **D₁** was exposed to pentane vapour diffusion under air and exposed to daylight at room temperature. After one day, yellow crystals of the derivative **D₁** started to grow along the wall of the flask and after one week the solution was almost colourless. The complex **D₁** can be then collected as a yellow polycrystalline material in a very good yield (up to 90–95%) [5,6]. However, if this work-up is conducted for a longer period (2 months) at room temperature in a sealed bottle in order to prevent solvent evaporation, tiny deep red crystals of the new derivative **1** (Fig. 2a) appeared slowly. Only a few crystals were formed preventing NMR characterization or elemental analyses to be performed. However, an X-ray diffraction study (Table 1) performed on a single crystal allowed the molecular structure of this unexpected compound to be established.



Scheme 1.

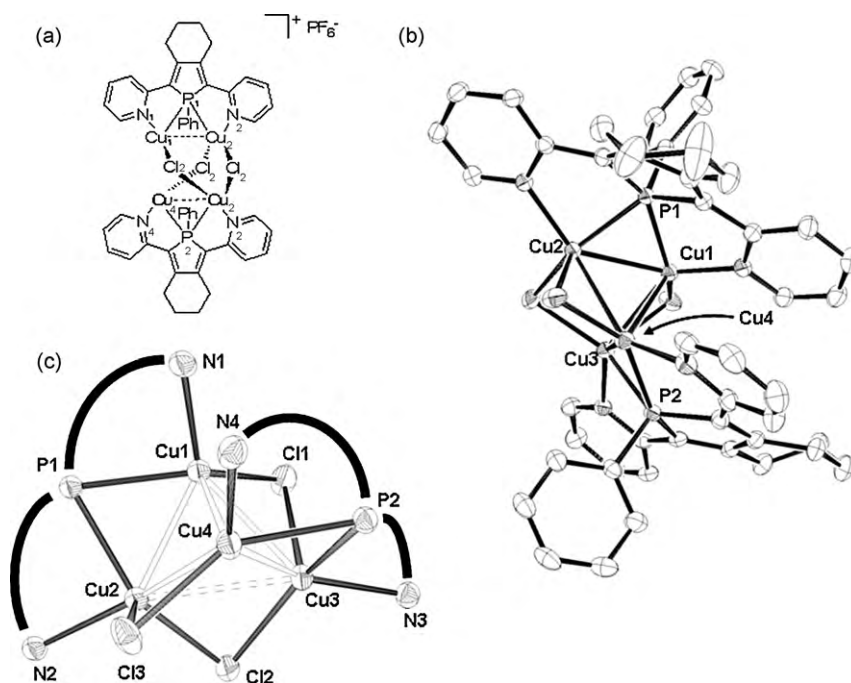


Fig. 2. (a) Chemical structure of derivative **1**; (b) Ortep view of the monocationic complex **1**; (c) view of the $[\text{Cu}_4\text{Cl}_3]$ core the complex **1**; the N,P,N ligands **B** are schematically represented by the black curved lines.

Table 1
Crystal data and structure refinement for derivative **1**.

	1. $\text{PF}_6^- \cdot 3\text{CH}_2\text{Cl}_2$
Molecular formula	$\text{C}_{99}\text{H}_{88}\text{Cl}_{12}\text{Cu}_8\text{F}_{12}\text{N}_8\text{P}_6$
CCDC number	763502
Molecular weight	2737.31
a (Å)	17.481(1)
b (Å)	14.082(2)
c (Å)	21.183(1)
α (°)	90
β (°)	90.762(1)
γ (°)	90
V (Å ³)	5214.1(8)
Z	2
D_c (g cm ⁻³)	1.744
Crystal system	Monoclinic
Space group	$P2_1/a$
Temperature (K)	120(2)
Wavelength Mo- $K\alpha$ (Å)	0.71069
Crystal size (mm)	$0.3 \times 0.3 \times 0.3$
μ (mm ⁻¹)	2.071
$F(000)$	2744
θ limit (°)	2.66–32.05
Index ranges hkl	$-26 \leq h \leq 26$ $-20 \leq k \leq 21$ $-31 \leq l \leq 31$
Reflections collected	32512
Independent reflections	18128
Reflections $[I > 2\sigma(I)]$	12825
Data/restraints/parameters	18128/0/668
Goodness-of-fit on F^2	1/029
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0499$ $wR2 = 0.1141$
R indices (all data)	$R1 = 0.0826$ $wR2 = 0.1280$
Largest diff peak and hole (e Å ⁻³)	1.227 and -1.337

Derivative **1** crystallizes in the $P2_1/a$ space group of the monoclinic system. The asymmetric unit contains one monocationic $\text{Cu}_4\text{Cl}_3(\mathbf{B})_2$ cluster (Fig. 2b), one PF_6^- anion and two dichloromethane molecules. The monocation of **1** is based on a highly distorted Cu_4 tetrahedron (Fig. 2c). The Cu–Cu distances lie in the range of those usually accepted for cuprophilic interactions between Cu(I) metal centers (Table 2) [6], except for the Cu(2)–Cu(3) distance (2.9540(9) Å), which is markedly longer (Table 2, Fig. 2c).

The three μ^2 -bridging chloride ligands Cl(1), Cl(2) and Cl(3) are linked to the Cu(1) and Cu(3), the Cu(2) and Cu(4), and the Cu(2) and Cu(4) metal centres, respectively (Fig. 1). The Cl(2) anion adopts a classical symmetrically μ^2 -bridging coordination mode ($\Delta d(\text{Cl}(2)\text{--Cu}) = 0.023$ Å; Cl(2)–Cu–Cu angles, 49.56(2)° and 50.24(2)°). In contrast, the Cl(1) and Cl(3) have a markedly unsymmetrical semi-bridging coordination mode ($\Delta d(\text{Cl}(1)\text{--Cu}) = 0.294$ Å; Cl(1)–Cu–Cu angles, 50.88(2)° and 61.53(2)°; $\Delta d(\text{Cl}(3)\text{--Cu}) = 0.267$ Å, Cl(3)–Cu–Cu angles, 49.67(2)° and 58.70(3)°). The coordination sphere of the Cu(1) metal centre is completed by two ligands **B** acting as 6-electron $\mu\text{-}1\kappa\text{N}:1,2\kappa\text{P}:2\kappa\text{N}$ donors with the the P(1) atom bridging the Cu(1) and Cu(3) centers and the P(2) atom bridging the Cu(2) and Cu(4) centers (Fig. 1). The geometric data of the bis(2-pyridyl)phosphole moieties in **1** (Table 3) are unremarkable and compare with those observed in other Cu(I)-complexes [5,6,9].

If the Cu–Cu interactions are ignored, the Cu(1) and Cu(4) metal centres have a T-shaped trigonal planar coordination sphere, whereas the Cu(2) and Cu(3) metal centres have a distorted tetrahedral geometry (Fig. 2c). It appears that complex **1** features an unprecedented

Table 2
Selected bond lengths [Å] and angles [°] for complex **1**.

M- μ P	M-N	M...M	M-Cl	N-M- μ P	M- μ P-M	μ P-M-M	μ Cl-M-M
2.2867(10)	2.014(3)	2.5226(7)	2.2083(9)	85.76(7)	67.15(3)	56.41(2)	50.88(2)
2.2875(9)	2.078(2)	2.5298(7)	2.2085(9)	86.40(7)	66.99(3)	56.44(2)	61.53(2)
2.2574(10)	2.037(3)	2.6317(8)	2.2817(9)	84.80(7)		55.45(2)	49.56(2)
2.3128(9)	2.053(2)	2.6506(8)	2.3046(9)	85.65(7)		57.55(2)	50.24(2)
		2.7492(8)	2.4753(10)				49.67(2)
		2.9540(9)	2.5023(10)				58.70(3)

Table 3
Selected bonds lengths [Å] and angles [°] of the bis(2-pyridyl)phosphole moieties in the free ligand **B** and in the derivative **1**.

	P-C ¹	C ¹ -C ²	C ² -C ⁷	C ⁷ -C ⁸	C ¹ -C _{Py}	C ¹ -P-C ⁸
	P-C ⁸				C ⁸ -C _{Py}	
B	1.806(6)	1.365(9)	1.478(9)	1.354(8)	1.466(9)	90.5(3)
	1.806(6)				1.467(8)	
1	1.805(3)	1.360(4)	1.459(4)	1.354(4)	1.459(4)	91.19(13)
	1.808(3)				1.461(4)	
	1.810(3)	1.358(4)	1.479(4)	1.363(4)	1.457(4)	90.86(13)
	1.813(3)				1.460(4)	

structure in which μ^2 -bridging phosphane ligands are coordinated to two Cu(I) centres having different (tri- and tetra-) coordination geometries (Cu(1) and Cu(4), 'P₁N₁Cl₁' environment; Cu(2) and Cu(3), the 'P₁N₁Cl₂' environment, Fig. 2c). Note that in all the other known Cu(I) complexes and the related supramolecular assemblies **G** [5,6,8], the metal centres always exhibit a tetracoordinated distorted tetrahedron geometry. The only other example of a dimer with a "mixed coordination geometry" involving a μ -P center is the Ag(I) dimer **E**₂ (tetra- and penta-coordinated Ag(I) centres) when associated with the Al[OC(CF₃)₃]₄⁻ counter-anion [7]. It is striking to note that in a highly unsymmetrical environment (mixed coordination centres in a highly distorted tetrahedral Cu₄Cl₃ core), the two μ^2 -P atoms are symmetrically bridging the Cu(I) centres (Δ (P(1)-Cu) = 0.001 Å, P(1)-Cu-Cu angles, 56.41(2)° and

56.44(2)°; Δ (P(2)-Cu) = 0.065 Å, P(2)-Cu-Cu angles, 55.45(2)° and 57.55(2)°). This result shows that there is no direct relation between the symmetry of the P-donor and that of the metal fragments.

It is interesting to compare the cationic complex **1** and the neutral complex **D**₂ (Fig. 1), obtained by reacting ligand **B** with CuCl in dichloromethane [6], that share structural similarities (Fig. 3). Complex **D**₂ (Fig. 3a) bears a fourth μ^2 -Cl ligand that formally replaces the uncoordinated PF₆⁻ counter-anion of **1** and connects the Cu(1) and Cu(4) metal centres [6]. The gross symmetry of the neutral complex **D**₂ is higher than the symmetry of the monocationic tetramer **1** (Fig. 3). In **D**₂, the four metal centre coordination spheres are 'P₁N₁Cl₂' distorted tetrahedrons. All the μ^2 -bridging chlorine anions are symmetrically bridging the metal centres (Cu-Cl bond lengths, 2.326(2) – 2.374(1) Å), and only two

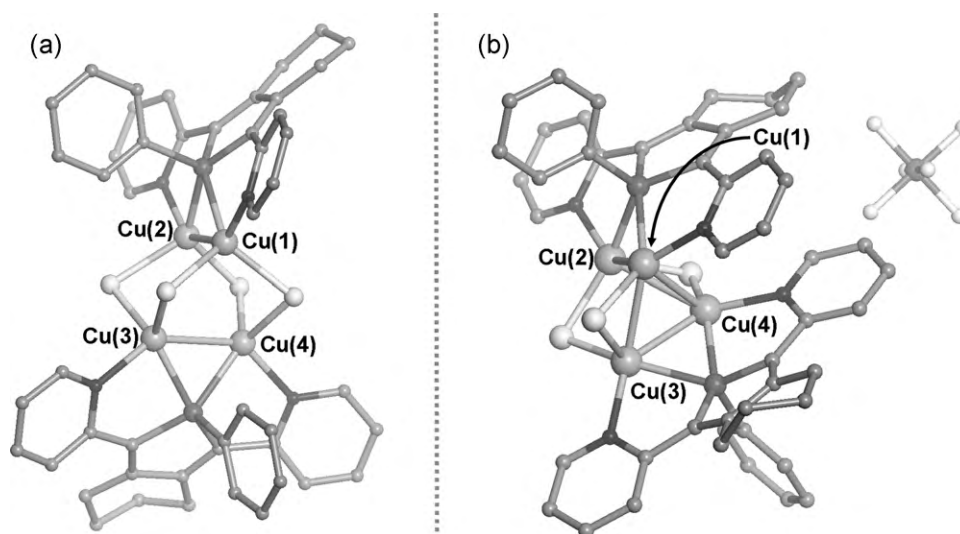


Fig. 3. Comparison between the solid state structure of (a) derivative **D**₂ [6] and (b) derivative **1**; in both cases, dichloromethane molecules included in the unit cell are not shown.

couples of Cu(I) metal centres (those bridged by the μ^2 -P atoms) are involved in cuprophilic interactions ($d(\text{Cu}-\text{Cu})=2.566(1)$ Å and $2.598(1)$ Å; the other Cu(I)–Cu(I) distances being longer than 3.18 Å). In the case of the complex **1** (Fig. 3b), the formal 'removal' of one bridging μ^2 -Cl ligand results in (i) a decrease of the symmetry of the Cu₄ central core compared to **D**₂ and (ii) an increase of the number of cuprophilic interactions (Fig. 3, Table 2). Most probably these cuprophilic interactions contribute to the stability of the monocationic Cu₄ cluster **1** whose formation is originally due to the geometric constraints accompanying the bridging phosphane mode of the ligand **B**.

The formation of complex **1** deserves a discussion since the only potential source of the μ^2 -Cl ligands in its Cu₄Cl₃ core is CH₂Cl₂, which is used as solvent. These Cl-ligands can be generated by two processes: activation of dichloromethane by the Cu(I) centers of **D**₂ or decomposition of dichloromethane by the sun light. Few examples of chlorine ions abstraction from CH₂Cl₂ mediated by Cu(I) complexes have been previously described [11] and the mechanism of this halide abstraction remains unclear. On the other hand, it has been shown that near UV irradiation of dichloromethane in presence of Cu(I) salts as catalyst causes its decomposition into HCl, C₂H₂Cl₄ and peroxides [12]. In this latter case, HCl would react with **D**₁ affording derivative **1** bearing μ^2 -Cl ligands. Since our crystallization experiments were performed in sunlight, these two processes can participate to the formation of complex **1**. Considering the long reaction time, it is very probable that the formation of complex **1** implies a very slow trapping reaction of the HCl formed upon CH₂Cl₂ decomposition by the Cu₂(**B**) moieties of **D**₁.

3. Conclusion

In this work, we describe the solid state structure of a new (Cu)₄ cluster **1** in which two ligands **B** act as a 6-electron μ -1 κ N:1,2 κ P:2 κ N donors with a symmetrically bridging P-donor. Derivative **1** is the first example of a mixed coordination Cu(I) complex assembled by μ -P centers. Interestingly, despite the fact that the Cu₄ core of derivative **1** is a highly unsymmetrical distorted tetrahedron, the two μ^2 -P ligands are symmetrically bridging the metal centres.

4. Experimental part

A CH₂Cl₂ solution (10 mL) of complex **D**₁ (0.050 g, 0.05 mmol) was stirred for 3 h at room temperature. This solution was transferred in glass tubes that were introduced in a glass bottle filled with pentane. This bottle was sealed and left at room temperature under daily light for two months. After one day, yellow crystals of **D**₁ start to grow in the CH₂Cl₂ solution along the wall of the glass tubes. After two months, a very few amount of tiny red crystals of **1** are observed on the wall of the glass tube close to the surface of the CH₂Cl₂ solution and can be collected for X-ray diffraction studies on single crystal.

CCDC reference number 763502 contains the supplementary crystallographic data for derivative **1**. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ,

UK; fax: (internat.) + 44 1223 336 033; e-mail: depos-it@ccdc.cam.ac.uk.

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