

## Exo-metal coordination by a tricyclic $[\{P(\mu\text{-N-2-NC}_5\text{H}_4)\}_2(\mu\text{-O})\}_2$ dimer in $[\{P(\mu\text{-N-2-NC}_5\text{H}_4)\}_2(\mu\text{-O})\}_2\{\text{CuCl}\cdot(\text{C}_5\text{H}_5\text{N})_2\}_4$ $\{2\text{-NC}_5\text{H}_4 = 2\text{-pyridyl}, \text{C}_5\text{H}_5\text{N} = \text{pyridine}\}^\dagger$

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The *in situ* reaction of the phosphazane dimer  $[\text{CIP}(\mu\text{-N-2-NC}_5\text{H}_4)]_2$  (**2**) with CuCl in the presence of  $\text{C}_5\text{H}_5\text{N}/\text{H}_2\text{O}$  gives the title complex  $[\{P(\mu\text{-N-2-NC}_5\text{H}_4)\}_2(\mu\text{-O})\}_2\{\text{CuCl}\cdot(\text{C}_5\text{H}_5\text{N})_2\}_4$  (**1**), containing a tricyclic  $[\{P(\mu\text{-N-2-NC}_5\text{H}_4)\}_2(\mu\text{-O})\}_2$  ligand which is isoelectronic with species of the type  $[\{P(\mu\text{-NR})\}_2\text{NR}]_2$ .

We have recently become interested in the synthesis and coordination chemistry of macrocycles of the type  $[\{P(\mu\text{-NR})\}_2(\mu\text{-NR}')\}_n$ , composed of four-membered  $[\text{P}(\text{NR})\text{NR}']_2$  ring units linked together into tricyclic arrangements by NR' groups (Fig. 1a).<sup>1,2</sup> The first representatives of this class of compounds were the dimeric macrocycles  $[\{P(\mu\text{-N}^i\text{Pr})\}_2(\mu\text{-N}^i\text{Pr})\}_2$ <sup>3</sup> and  $[\{P(\mu\text{-N}^i\text{Bu})\}_2(\mu\text{-N}^i\text{Bu})\}_2$ .<sup>4</sup> More recently, however, we were able to show that larger macrocycles of this type can be prepared where less sterically demanding NH groups bridge the dimeric ring constituents together, the tetrameric macrocycle  $[\{P(\mu\text{-N}^i\text{Bu})\}_2\text{NH}]_4$  being obtained almost quantitatively from the condensation reaction of  $[\text{CIP}(\mu\text{-N}^i\text{Bu})\text{NH}]_2$  with  $[\text{H}_2\text{NP}(\mu\text{-N}^i\text{Bu})\text{NH}]_2$ .<sup>1</sup> A minor product in the latter reaction is the host-guest complex  $[\{P(\mu\text{-N}^i\text{Bu})\}_2\text{NH}]_5\cdot\text{HCl}$ , containing the pentameric homologue  $[\{P(\mu\text{-N}^i\text{Bu})\}_2\text{NH}]_5$ .<sup>2</sup> We present here the synthesis and structure of  $[\{P(\mu\text{-N-2-NC}_5\text{H}_4)\}_2(\mu\text{-O})\}_2\{\text{CuCl}\cdot(\text{C}_5\text{H}_5\text{N})_2\}_4$  (**1**), containing the first example of an isoelectronic, oxygen-bridged cyclic species  $[\{P(\mu\text{-N-2-NC}_5\text{H}_4)\}_2(\mu\text{-O})\}_2$  of this type (Fig. 1b). Complex **1** exhibits unprecedented *exo*-coordination of four Cu<sup>I</sup> centres by the P atoms of the ring.

$[\{P(\mu\text{-N-2-NC}_5\text{H}_4)\}_2(\mu\text{-O})\}_2\{\text{CuCl}\cdot(\text{C}_5\text{H}_5\text{N})_2\}_4$  (**1**) is obtained by the reaction of  $[\text{CIP}(\mu\text{-N-2-NC}_5\text{H}_4)]_2$  (**2**)<sup>5</sup> in the presence of a stoichiometric amount of  $\text{H}_2\text{O}$  (added as a standard solution in pyridine) (Scheme 1) (ESI †). This procedure gives **1** in relatively low though reproducible yield (27%). Significantly, repeating the reaction in the absence of CuCl gave an intractable mixture of many products [as observed by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy ( $\delta$ 0–160)]. It therefore appears

that coordination of the P<sup>III</sup> centres of **2** during or prior to reaction with  $\text{H}_2\text{O}$  has an important structure directing influence. A possible explanation for this is the steric effect of metal coordination. This effect presumably also prevents oligomerisation of the ring units of **2** into an otherwise more thermodynamically stable adamantane structure.<sup>3</sup> The reactivity pattern observed in the formation of **1** contrasts with that found for reactions of uncoordinated **2** with RNHLi, where the lower steric congestion results in rearrangement and the adoption of an adamantane-forming reaction pathway.<sup>5</sup> Solutions of **1** are highly air-sensitive and thermally unstable, thermolysis or oxidation resulting in disproportionation into the Cu<sup>II</sup> complex  $[\text{CuCl}_2\cdot 4\text{C}_5\text{H}_5\text{N}]$  (**3**) (characterised by X-ray crystallography, ESI†) and Cu<sup>0</sup>. **3** is often obtained as a minor contaminant in isolated samples of **1**. The IR spectrum of solid **1** shows a strong band at  $932\text{ cm}^{-1}$  for the P–O–P group (absent in the IR of **2**), while the  $^{31}\text{P}$  NMR behaviour of **1** in  $\text{C}_5\text{H}_5\text{N}$  is consistent with partial dissociation into  $[\{P(\mu\text{-N-2-NC}_5\text{H}_4)\}_2(\mu\text{-O})\}_2\{\text{CuCl}\cdot 2\text{C}_5\text{H}_5\text{N}\}_n$  ( $n = 0\text{--}3$ ) and  $[\text{CuCl}\cdot(\text{C}_5\text{H}_5\text{N})_{3,4}]$ .<sup>6</sup> At  $+25\text{ }^\circ\text{C}$ , a saturated solution shows a singlet for intact **1** [ $\delta -4.12$  (s.) (*ca.* 50%)] and two multiplets [ $\delta -3.03$  (mult.),  $-4.56$  (d.),  $^2J_{\text{P-(N,O)-P}} = 22$  Hz)]. At  $-30\text{ }^\circ\text{C}$ , the latter resonances separate into two doublets [ $\delta -1.87$  (d.),  $3.96$  (d.),  $^2J_{\text{P(N,O)P}} = 22$  Hz, *i.e.*, 1,2-, 1,3 or 1,4-coordinated  $[\{P(\mu\text{-N-2-NC}_5\text{H}_4)\}_2(\mu\text{-O})\}_2\{\text{CuCl}\cdot 2\text{C}_5\text{H}_5\text{N}\}_2$ ] and two, poorly-resolved minor resonances [ $\delta -2.58$  (mult.) and  $-4.16$  (mult.)]. Addition of excess CuCl to a saturated solution of **1** results in one major singlet at  $\delta -7.34$ , possibly suggesting suppression of the fragmentation process.

The low-temperature X-ray study of **1**·6pyridine shows that the complex has a centrosymmetric molecular structure, composed of the tricyclic dimer  $[\{P(\mu\text{-N-2-NC}_5\text{H}_4)\}_2(\mu\text{-O})\}_2$  which coordinates four Cu<sup>I</sup> ions using the P<sup>III</sup> centres (Fig. 2) (ESI†). In addition, there are six pyridine molecules per molecule of **1** present in the crystal lattice. The arrangement of the  $[\{P(\mu\text{-N-2-NC}_5\text{H}_4)\}_2(\mu\text{-O})\}_2$  unit of **1** is the same as that found for the dimeric species  $[\{P(\mu\text{-NR})\}_2(\mu\text{-NR})\}_2$  ( $\text{R} = \text{Bu}, \text{Pr}$ ),<sup>3,4</sup> in which the four-membered  $[\text{P}(\mu\text{-NR})\text{NR}]_2$  ring units are connected by NR groups. However, the tricyclic  $[\{P(\mu\text{-N-2-NC}_5\text{H}_4)\}_2(\mu\text{-O})\}_2$  core of **1** represents the first example of an isoelectronic arrangement containing O-bridged  $[\text{P}(\mu\text{-NR})\text{NR}]_2$  units.

Within the  $[\{P(\mu\text{-N-2-NC}_5\text{H}_4)\}_2(\mu\text{-O})\}_2$  unit of **1**, the P–N bond lengths [range  $1.702(3)\text{--}1.722(2)$  Å] and P–N–P and P–N–O angles [mean  $99.9$  and  $80.0^\circ$ , respectively] are little changed from those found in the dimer  $[\text{CIP}(\mu\text{-N-2-NC}_5\text{H}_4)]_2$  (**2**),<sup>5</sup> despite the incorporation of these units into a cyclic framework and the coordination of the P centres to Cu<sup>+</sup> ions. The geometry at the dimer-bridging O centres of the  $[\{P(\mu\text{-N-2-NC}_5\text{H}_4)\}_2(\mu\text{-O})\}_2$  unit [ $\text{P}(1)\text{--O}(1)\text{--P}(2\text{A})$   $136.5(1)^\circ$ ] is very similar to that of the dimer-bridging NR groups in  $[\{P(\mu\text{-NR})\}_2(\mu\text{-NR})\}_2$  ( $\text{R} = \text{Pr}, \text{Bu}^4$ ) [*e.g.*, for  $\text{R} = \text{Bu}$ , P–N–P  $136.7(2)^\circ$ ].<sup>4</sup> The shortness of the P–O bonds in **1** [mean  $1.64$  Å] and the acuteness of the N–P–O angles [mean  $105.5^\circ$ ], compared to the corresponding bond lengths and angles in

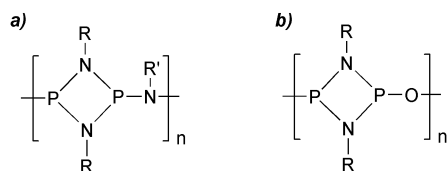
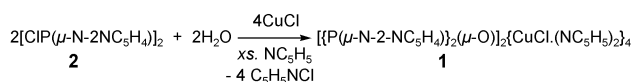
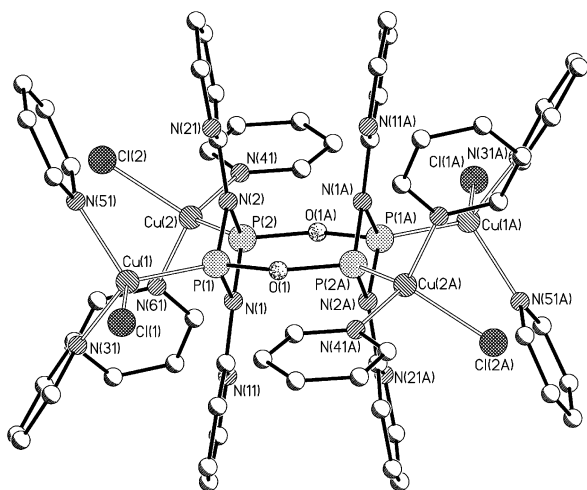


Fig. 1 Connectivity in isoelectronic macrocycles of the type  $[\{P(\mu\text{-NR})\}_2(\mu\text{-X})\}_n$  ( $\text{X} = \text{NR}'$  or O).



Scheme 1

† Electronic supplementary information (ESI) available: synthesis of compound **1**, crystal data for compounds **1** and **3** and structure of compound **3**. See <http://www.rsc.org/suppdata/cc/b3/b309842g/>



**Fig. 2** Structure of **1**. H-atoms and pyridine molecules present in the lattice have been omitted for clarity. Key bond lengths (Å) and angles (°): P(1)–N(1) 1.722(2), P(1)–N(2) 1.708(3), P(1)–O(1) 1.636(2), P(1)–Cu(1) 2.1482(8), P(2)–N(1) 1.702(3), P(2)–N(2) 1.713(2), P(2)–O(1A) 1.648(2), P(2)–Cu(2) 2.1308(9), Cu(1)–Cl(1) 2.291(1), Cu–N mean 2.08, Cu(2)–Cl(2) 2.314(1), O(1)⋯O(1A) 3.84,  $P_2N_2$  centroid⋯ $P_2N_2$  centroid 3.05, P(1)–N(1)–P(2) 99.8(1), N(1)–P(1)–N(2) 79.8(1), P(1)–N(2)–P(2) 100.0(1), N(1)–P(2)–N(2) 80.2(1), N–P–O mean 105.5, P(1)–O(1)–P(2A) 136.5(1).

$[\{P(\mu-NR)\}_2(\mu-NR)]_2$ ,<sup>3,4</sup> results in a significantly smaller macrocyclic cavity for the  $[\{P(\mu-N-2-NC_5H_4)\}_2(\mu-O)]_2$  ligand. This is reflected in both the distance between the mean planes of the two  $P_2N_2$  rings [*ca.* 3.05 Å] and the distance between the two O centres [*ca.* 3.84 Å] in the  $[\{P(\mu-N-2-NC_5H_4)\}_2(\mu-O)]_2$  ligand [*cf.* *ca.* 3.75 and 4.07 Å, respectively, for the corresponding dimensions in  $[\{P(\mu-N^tBu)\}_2(\mu-N^tBu)]_2$ ].<sup>4</sup> The near planarity of the  $P_2N_2$  rings of the  $[\{P(\mu-N-2-NC_5H_4)\}_2(\mu-O)]_2$  ligand is in common with the  $P_2N_2$  ring unit of the precursor **2**<sup>5</sup> and appears to be a simple consequence of the low steric demands of the 2-NC<sub>5</sub>H<sub>5</sub> substituents. In contrast, the greater steric demands of the <sup>t</sup>Bu and <sup>i</sup>Pr groups in  $[\{P(\mu-NR)\}_2(\mu-NR)]_2$  result in puckered  $P_2N_2$  ring units.<sup>3,4</sup> The Cu–P bond lengths in **1** [mean P–Cu 2.14 Å] and the distorted tetrahedral geometries of the Cu<sup>I</sup> ions are typical of previously reported Cu–P bonded species.<sup>7</sup> However, there have been no previous reports of such *exo*-metal coordination for the related  $[\{P(\mu-NR)\}_2(\mu-NR)]_2$  dimers and this is the first observation of such coordination for this class of ligands. The closest situation to **1** is found in the behaviour of the cyclic, P–O–P bonded species  $[(R_2N)_2PO]_n$  (*n*

= 3–6), which are known to coordinate transition metals using their P centres.<sup>8</sup>

In summary, this study discloses the first representative of a class of O-bridged ligands of the type  $[\{P(\mu-NR)\}_2(\mu-O)]_n$ , the arrangement found in **1** being isoelectronic with the well known phosphazane dimers  $[\{P(\mu-NR)\}_2(\mu-NR)]_2$ . The *exo*-metal coordination found in **1** is the first observation of such bonding for this class of ligands, and represents a potential means by which the extent and nature of oligomerisation can be controlled in such species.

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