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# Halide and substituent dependent structural variation in copper(I) halide-complexes of 1,5,9-triphosphacyclododecanes

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The reactions of 1,5,9-triethyl-1,5,9-triphosphacyclododecane, [12]-ane-P<sub>3</sub>Et<sub>3</sub>, and 1,5,9-tri(2-propyl)-1,5,9-triphosphacyclododecane, [12]-ane-P<sub>3</sub><sup>i</sup>Pr<sub>3</sub> with copper(I)halides produce either bimetallic species of the type [(12]-ane-P<sub>3</sub>R<sub>3</sub>)Cu(CuX<sub>2</sub>)] (X = halide) or monomeric [(12]-ane-P<sub>3</sub>R<sub>3</sub>)CuX] depending on the nature of the halide and, to a lesser extent, the macrocycle. With CuCl only bimetallic complexes are formed with one copper centre bound to the macrocycle and a second attached through a Cu-Cu bond with a mono bridging chloride. CuBr affords monomeric [(12]-ane-P<sub>3</sub>R<sub>3</sub>)CuBr] complexes when performed in a 1:1 M:L ratio whereas the bimetallic compound [(12]-ane-P<sub>3</sub>Et<sub>3</sub>)(CuBr)<sub>2</sub>], resulted when a 2:1 ratio of M:L was employed. With CuI in all ratios only monomeric complexes were obtained. The synthesised complexes have been fully characterised by spectroscopic and analytical techniques and by determination of the molecular structures by single-crystal X-ray diffractometry.

## Introduction

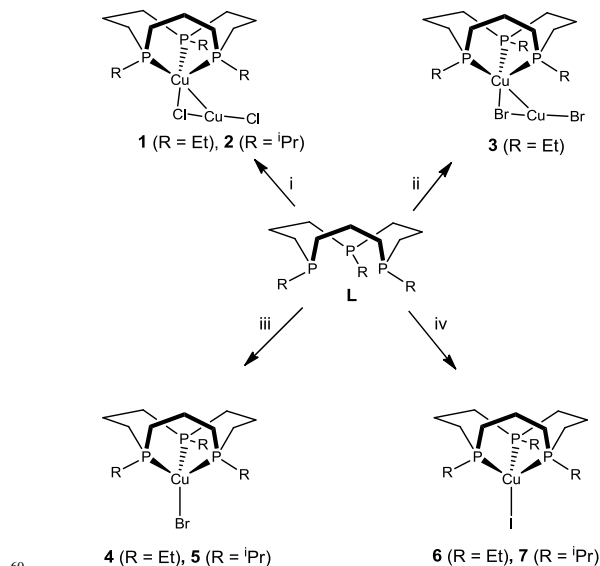
Although the literature concerning phosphorus ligands and their metal complexes is extensive, coverage of macrocyclic systems containing solely P-donors is sparse; triphospha derivatives are particularly poorly represented. Part of the reason for this lies in the difficulty of their preparation which is predominantly by template methods and although 9-, 10- and 11-membered systems are known,<sup>1</sup> their chemistry has been restricted by the inability to release them (at least intact or unchanged) from the metal template used for their construction. Of the known triphosphamacrocycles, 1,5,9-triphosphacyclododecanes ([12]-ane-P<sub>3</sub>R<sub>3</sub>) are the class that has received the greatest attention;<sup>2</sup> this merely reflects the fact that methods are known for their liberation.<sup>2f</sup> We have refined synthetic methods for the preparation and functionalisation of these tridentate macrocycles allowing the *exo*-substituent (R in [12]-ane-P<sub>3</sub>R<sub>3</sub>) to be varied from simple alkyls through aryl derivatives to donor functionalised systems and the coordination chemistry of these ligands has been extensively explored by us.<sup>2a-f</sup> Much of the focus of these studies has been on octahedral metal complexes with one exception of a four-coordinate, pseudo-tetrahedral Ni(II) complex.<sup>3</sup> Complexes with coordination numbers <4 are unprecedented.

Like their 12-membered triaza and trithia relatives, 12aneP<sub>3</sub>R<sub>3</sub> ligands may be versatile in their coordination mode and can bind as bi- or mono-dentate ligands. Arising from flexibility in the 3-carbon backbone bridge between adjacent P-donors, in the κ<sup>3</sup>-coordination mode the chelate bite angle is flexible showing a P-M-P range from 81° in Ti([12]-ane-P<sub>3</sub>Et<sub>3</sub>)Cl<sub>3</sub><sup>2b</sup> to 126° for one of the angles in [Ni([12]-ane-P<sub>3</sub>Et<sub>3</sub>)Br]Br.<sup>3</sup> Given that examples of [12]-ane-P<sub>3</sub>R<sub>3</sub> complexed to metal ions that prefer tetrahedral coordination are currently unknown and that this inherent ligand flexibility should facilitate accommodation of such metal ions, we sought to investigate the coordination chemistry of [12]-ane-P<sub>3</sub>Et<sub>3</sub> and [12]-ane-P<sub>3</sub><sup>i</sup>Pr<sub>3</sub> with closed-shell, d<sup>10</sup> copper(I), a metal ion with a strong preference for forming tetrahedral complexes. We

have chosen the triethyl and tri(*iso*-propyl) P<sub>3</sub> macrocycles to explore influences upon co-ordination properties. The latter is expected to be the more sterically encumbered which might lead to exclusive formation of monomeric species whereas the slighter 12aneP<sub>3</sub>Et<sub>3</sub> might be less discriminating and allow formation of bimetallic species.

## Results and Discussion

### Solid state structures



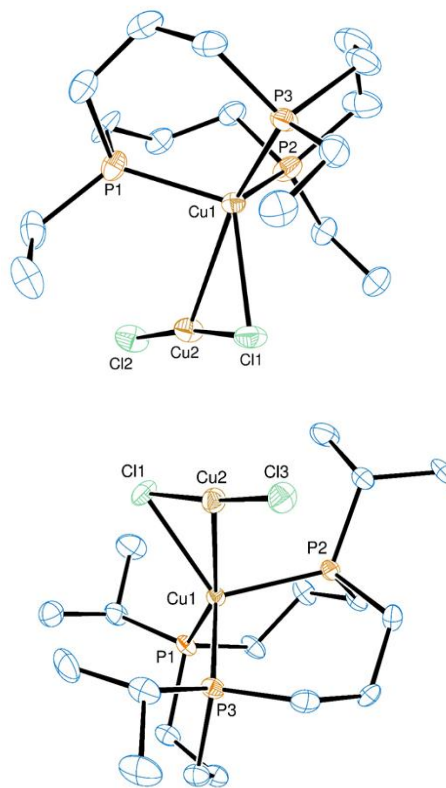
Scheme 1. i) 1:1 or 2:1 CuCl:L; ii) 2:1 CuBr:L; iii) 1:1 CuBr:L; iv) 1:1 CuI:L.

Overall reaction methodology and outcomes, and structures of the new compounds are presented in Scheme 1. The addition of 1 mole equivalent of CuCl to [12]-ane-P<sub>3</sub>Et<sub>3</sub> or [12]-ane-P<sub>3</sub><sup>i</sup>Pr<sub>3</sub> in dichloromethane at room temperature gave, after work-up and recrystallization, white solids with the unexpected compositions of [(12]-ane-P<sub>3</sub>Et<sub>3</sub>)Cu<sub>2</sub>Cl<sub>2</sub>], **1** and [(12]-ane-P<sub>3</sub><sup>i</sup>Pr<sub>3</sub>)Cu<sub>2</sub>Cl<sub>2</sub>], **2**. IR

and analytical data are consistent with the formulations and are otherwise unremarkable, as is also the case for all other new compounds reported here. The L:Cu ratio of 1:2 suggested the formation of either a salt of the nature of  $\{[12]\text{-ane-P}_3\text{R}_3\text{Cu}\}^+[\text{CuCl}_2]^-$  or a binuclear complex with the latter being confirmed in the solid-state upon determination of the molecular structures by single-crystal X-ray techniques (Figure 1). The binuclear structures consist of five coordinate copper atoms bonded to  $\kappa^3\text{-}[12]\text{-ane-P}_3\text{Et}_3$  or  $\kappa^3\text{-}[12]\text{-ane-P}_3^i\text{Pr}_3$  and a  $\kappa^2\text{-CuCl}_2$  unit with Cu(1)-Cu(2) distances of 2.7627(6) Å and 2.7001(11) Å for **1** and **2** respectively. The Cu(I)-Cu(I) interactions are supported by a single chloride bridge which is a unique motif for unsymmetrical Cu(I)-Cu(I) systems. Cu-Cu  $d^{10}\text{-}d^{10}$  bonding interactions are now well known but the Cu-Cu bond distances in **1** and **2** are shorter than in the  $[\text{Cu}_2\text{Br}_3]^{3-}$  anion which has a Cu-Cu bond of 2.837(4) Å<sup>4</sup> and the unsupported Cu-Cu bonds reported by Siemeling {Cu-Cu = 2.810(2) Å} and Stavropoulos {Cu-Cu = 2.905(3) Å}.<sup>5</sup> They are, however, appreciably longer than those reported for various reported organometallic dimeric and higher oligomeric and/or cluster compounds of Cu(I) and small copper chain compounds.<sup>6</sup> If the side-on ( $\eta^2$ ) bonded  $\text{CuCl}_2$  fragment is considered to occupy a single co-ordination site, the copper bound by the macrocycle has a pseudo-tetrahedral environment in **1** and **2**. The second copper atom in the  $\text{CuCl}_2$  group tends towards linear co-ordination geometry as is well known for anions of the type  $[\text{CuX}_2]^-$ , deviations from linearity vary from about 7° to 8° (Cl-Cu-Cl is 172.16(4) in **1** and 173.04(8) in **2**) no doubt arising from the unsymmetrical bonding configuration. As the *iso*-propyl group is more sterically demanding than ethyl,  $\kappa^3\text{-}[12]\text{-ane-P}_3^i\text{Pr}_3$  is anticipated to be more sterically encumbered than  $\kappa^3\text{-}[12]\text{-ane-P}_3\text{Et}_3$ . Contrary to expectation however, the Cu-Cu bond length is shorter in **2** than in **1**. Hence sterics appear to play little part in structurally perturbing the  $[\text{CuCl}_2]^-$  ligand, an observation further supported by the almost identical Cu(1)- $\mu\text{Cl}$  bond lengths in the two bimetallic complexes. It is noteworthy that these bonds are longer than those reported for related mononuclear tridentate phosphine copper chloride systems such as  $[\text{Cu}(1,1,1\text{-tris(diphenylphosphinomethyl)ethane})\text{Cl}]$ .<sup>7</sup> Thus, an electronic explanation for the shorter and presumably stronger Cu-Cu interaction in the more sterically encumbered **2** is likely responsible and might arise from the anticipated stronger  $\sigma$ -donating ability of the bulkier <sup>i</sup>Pr substituted ligand (albeit this is very slight).

Unlike the chloride complexes, the 1:1 reaction of either of the ligands with CuBr did not furnish a bimetallic complex, and only when the ratio was increased to 2:1 in favour of the metal salt and solely with  $[12]\text{-ane-P}_3\text{Et}_3$  was a dimeric species, **3**, isolated. The gross molecular structure of the bimetallic bromide **3** is analogous to that already described for **1** and **2** (figure 2). Closer inspection does reveal some differences between the bromo complex **3** and the two chloro bridged analogues with the Cu-Cu bond distance being unexpectedly shorter {2.6778(12) Å} than either of those in **1** and **2**. This shorter Cu-Cu distance coincides with a more acute Cu(1)-Br(1)-Cu(2) angle of 67.77(3)° compared to 74.72(3)° and 72.80(6)°; this compression more than compensates for the longer Cu(1)-Br bond length compared to the analogous Cu(1)-Cl bonds in **1** and **2**. Again the X-Cu-X unit is only slightly bent away from linearity, the Br-Cu(2)-Br angle of 170° is similar to the Cl-Cu(2)-

Cl angles of 172°/173° in **1** and **2**.



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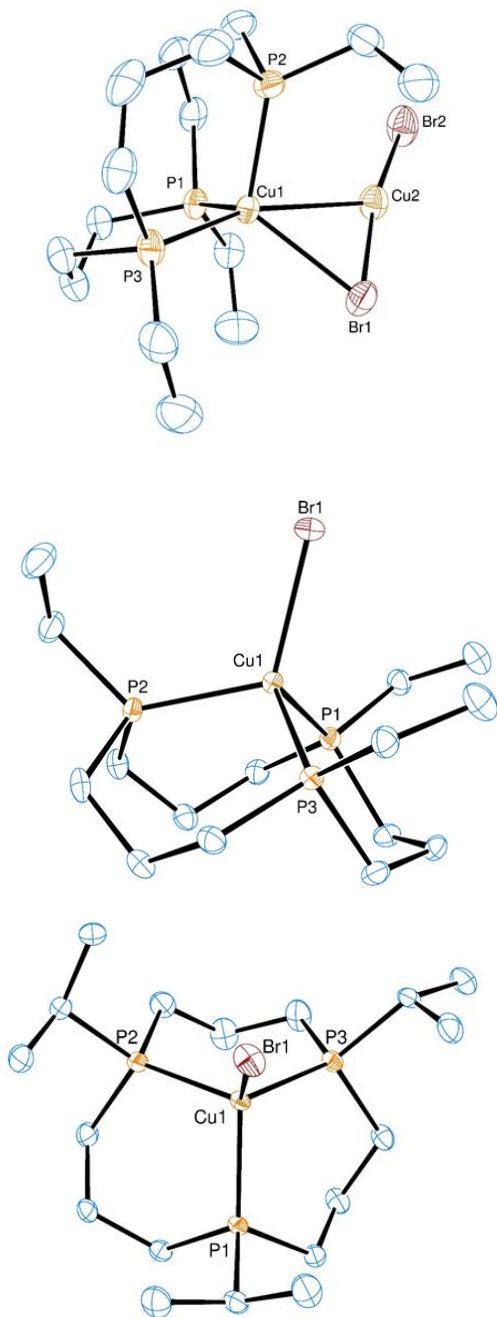
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**Figure 1.** Ortep views of the molecular structure of the bimetallic complexes **1** (top) and **2** (bottom). Hydrogens and one disordered (Cl1a, C2a and C3a) component for **1** are omitted for clarity. Selected bond lengths (Å) and angles (°) for **1**: P(1)-Cu(1) 2.2443(11), P(2)-Cu(1) 2.2443(11), P(3)-Cu(1) 2.2492(10), Cl(1)-Cu(2) 2.1369(11), Cl(1)-Cu(1) 2.4024(10), Cl(2)-Cu(2) 2.1143(11), Cu(1)-Cu(2) 2.7627(6), Cu(2)-Cl(1)-Cu(1) 74.72(3), P(2)-Cu(1)-P(1) 104.56(4), P(2)-Cu(1)-P(3) 103.24(4), P(1)-Cu(1)-P(3) 104.41(4), Cl(1)-Cu(1)-Cu(2) 48.26(3), Cl(2)-Cu(2)-Cl(1) 172.16(4), Cl(2)-Cu(2)-Cu(1) 130.66(4), Cl(1)-Cu(2)-Cu(1) 57.02(3), Cu2-Cl1-Cu1 74.72(3); and for **2**: P(1)-Cu(1) 2.2383(17), P(2)-Cu(1) 2.2471(18), P(3)-Cu(1) 2.2416(18), Cl(1)-Cu(2) 2.1359(19), Cl(1)-Cu(1) 2.4002(19), Cu(2)-Cl(3) 2.1071(19), Cu(2)-Cu(1) 2.7001(11), Cu(2)-Cl(1)-Cu(1) 72.80(6), Cl(3)-Cu(2)-Cl(1) 173.04(8), Cl(3)-Cu(2)-Cu(1) 128.74(7), Cl(1)-Cu(2)-Cu(1) 58.12(5), P(1)-Cu(1)-P(3) 104.71(7), P(1)-Cu(1)-P(2) 106.11(7), P(3)-Cu(1)-P(2) 104.73(7), Cl(1)-Cu(1)-Cu(2) 49.08(5).

The 1:1 reaction of CuBr with both  $[12]\text{-ane-P}_3\text{Et}_3$  and  $[12]\text{-ane-P}_3^i\text{Pr}_3$  gave the mononuclear complexes  $[(12)\text{-ane-P}_3\text{Et}_3\text{CuBr}]$ , **4** and  $[(12)\text{-ane-P}_3^i\text{Pr}_3\text{CuBr}]$  **5**. Unlike the triethyl macrocycle the 2:1 reaction of CuBr and  $[12]\text{-ane-P}_3^i\text{Pr}_3$  produced only **5** with no evidence of dimer formation. That the 2:1 mole ratio reaction of CuBr with  $[12]\text{-ane-P}_3^i\text{Pr}_3$  does not give rise to bi-nuclear species implies that a steric hindrance does come into play with the larger bromide and <sup>i</sup>Pr functions. The molecular structures of the two monomeric bromo complexes (figure 3) share many features with the bimetallic complexes discussed above with the copper centres being distorted tetrahedral with Cu-P bond lengths averaging 2.250(1) Å (**4**) and 2.252(1) Å (**5**) and chelate bite angles averaging 103.2(1)° and 103.1(1)° respectively. The Cu-Br bond lengths are similar to the related 4-co-ordinate Cu(I) bromo phosphine complex,  $\text{CuBr}(\text{C}_{10}\text{H}_8\text{N}_2)\{\text{P}(\text{C}_6\text{H}_5)_3\}$  in which Cu-Br = 2.428(3)

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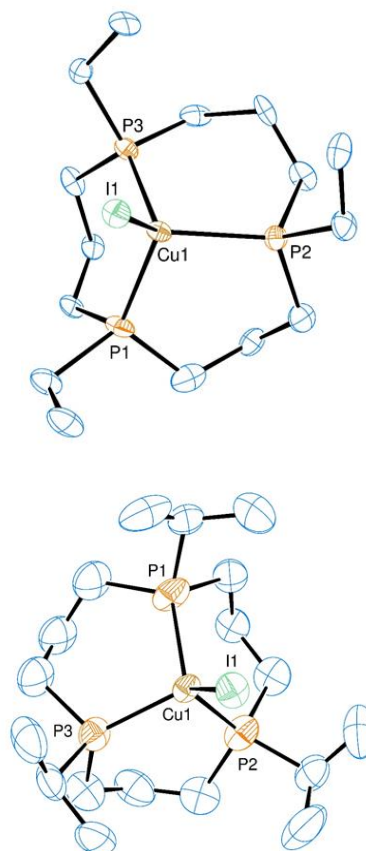
Å. The P-Cu-Br bond angles of  $115 \pm 1.5^\circ$  are similar to those in the other macrocycle complexes reported here and the Cu-P distances are comparable with those reported for tripodal phosphine complexes of CuBr<sup>8</sup> and it is clear that there is little difference in the coordination behaviour of the two macrocycles towards CuBr.



**Figure 2.** Ortep views of the molecular structure of the bimetallic complex **3** (top) and monomeric **4** (middle) and **5** (bottom). Hydrogens and one disordered component for **3** are omitted for clarity. Selected bond lengths (Å) and angles (°) for **3**: Cu(1)-P(3) 2.2396(15), Cu(1)-P(1) 2.2537(15), Cu(1)-P(2) 2.2551(16), Cu(1)-Br(1) 2.5267(9), Cu(1)-Cu(2) 2.6778(12), Cu(2)-Br(2) 2.2344(12), Cu(2)-Br(1) 2.2595(12), P(3)-Cu(1)-P(1) 105.02(6), P(3)-Cu(1)-P(2) 104.30(7), P(1)-Cu(1)-P(2) 104.08(6),

Br(1)-Cu(1)-Cu(2) 51.36(3), Br(2)-Cu(2)-Br(1) 169.71(5), Br(2)-Cu(2)-Cu(1) 129.42(5), Br(1)-Cu(2)-Cu(1) 60.86(3), Cu(1)-Br(1)-Cu(2) 67.77(3); for **4**: Br(1)-Cu(1) 2.4301(10), Cu(1)-P(2) 2.2477(16), Cu(1)-P(3) 2.2509(17), Cu(1)-P(1) 2.2520(17), P(2)-Cu(1)-P(3) 103.20(6), P(2)-Cu(1)-P(1) 102.72(6), P(3)-Cu(1)-P(1) 103.65(6), P(2)-Cu(1)-Br(1) 115.77(5), P(3)-Cu(1)-Br(1) 113.46(5), P(1)-Cu(1)-Br(1) 116.35(5) and for **5**: P(1)-Cu(1) 2.2483(7), P(2)-Cu(1) 2.2477(7), P(3)-Cu(1) 2.2592(7), Cu(1)-Br(1) 2.4410(4), P(2)-Cu(1)-P(1) 102.36(3), P(2)-Cu(1)-P(3) 103.76(3), P(1)-Cu(1)-P(3) 103.14(3), P(2)-Cu(1)-Br(1) 114.66(2), P(1)-Cu(1)-Br(1) 115.52(2), P(3)-Cu(1)-Br(1) 115.64(2).

The reaction of either P<sub>3</sub> macrocycle with CuI in 1:1 or 2:1 M:L ratios gave only mononuclear complexes of the type [Cu(L)I]. X-ray crystal structures of **6** and **7** (Figure 4) are completely analogous to those of **4** and **5** except for the obvious lengthening of the Cu-X bond in the iodides.



**Figure 3.** Ortep views of the molecular structure of the complexes **6** (top) and **7** (bottom). Hydrogens are omitted for clarity. For **7**, each of the C<sub>3</sub> bridges connecting adjacent phosphorus atoms is disordered, the conformation option of lower relative occupancy is omitted in each case for clarity. Selected bond lengths (Å) and angles (°) for **6**: P(1)-Cu(1) 2.243(2), P(2)-Cu(1) 2.252(11), P(3)-Cu(1) 2.235(11), Cu(1)-I(1) 2.5943(10), P(3)-Cu(1)-P(1) 103.3(4), P(3)-Cu(1)-P(2) 104.25(8), P(1)-Cu(1)-P(2) 103.4(4), P(3)-Cu(1)-I(1) 114.6(3), P(1)-Cu(1)-I(1) 115.15(7), P(2)-Cu(1)-I(1) 114.7(3); and for **7**: P(1)-Cu(1) 2.249(2), P(2)-Cu(1) 2.251(2), P(3)-Cu(1) 2.241(2), Cu(1)-I(1) 2.5881(9), P(3)-Cu(1)-P(1) 102.98(9), P(3)-Cu(1)-P(2) 101.23(9), P(1)-Cu(1)-P(2) 103.03(9), P(3)-Cu(1)-I(1) 115.59(7), P(1)-Cu(1)-I(1) 114.28(8), P(2)-Cu(1)-I(1) 117.66(7).

### Solution studies

The formation of binuclear or mononuclear complexes depending

upon the stoichiometry, nature of halide and substituent on phosphorus raises the question of whether the bimetallic complex is stable only in the solid-state. Dissociation would likely lead to  $\{([12]\text{-ane-P}_3\text{Et}_3)\text{Cu}\}^+$  and  $[\text{CuCl}_2]^-$  ions which would be expected to be temperature dependent. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3** shows a single broad peak at -28.1 ppm which compares with a value of -28.7 ppm for the monomeric bromide **4** with both showing a small downfield coordination shift of ~4 ppm. The broadening seen in the  $^{31}\text{P}\{^1\text{H}\}$  spectra extends to the  $^1\text{H}$  NMR spectra of both **3** and **4** which are closely similar with the  $\text{PCH}_2\text{R}$  and  $\text{PCH}_2\text{CH}_2\text{R}$  resonances occurring around 1.90 and 1.60 ppm respectively and the *exo* ethyl groups being represented by broad signals at ~1.65 and 1.15 ppm. However, little can be deduced from this as inspection of the spectra for all the synthesised complexes shows little variation with the  $[12]\text{-ane-P}_3\text{Et}_3$  complexes having  $^{31}\text{P}$  NMR shifts of  $-29 \pm 1$  ppm and the  $[12]\text{-ane-P}_3\text{iPr}_3$  complexes having  $\delta_{\text{P}}$  values of  $-21 \pm 2$  ppm. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are equally undistinguished with resonances in essentially the same regions for all complexes (excepting differences in the nature of the *exo*-substituents between the two macrocycles). The broadness of the resonances is presumably due in part to the effect of the electric quadrupole moment of  $\text{Cu}^{\text{II}}$  and cooling samples to  $-70$  °C produced some peak sharpening in their  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra but without significant changes in the chemical shifts implying the absence of facile dissociation of either macrocycle or  $\text{CuX}_2$ . Solvent effects are also small as dissolution in  $\text{CD}_3\text{CN}$  (the compounds are poorly soluble) or  $(\text{CD}_3)_2\text{CO}$  (slightly soluble) did not give any observable change in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra suggesting retention of the halide and/or  $\text{CuX}_2$  fragment. Attempts to isolate compounds of the general formula  $\{([12]\text{-ane-P}_3\text{R}_3)\text{Cu}(\text{MeCN})\}\text{X}$  from the 1:1 reaction of the triphosphorus macrocycles with  $[\text{Cu}(\text{MeCN})_4]\text{X}$  were unsuccessful. Monitoring the reactions by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy revealed complex mixtures from which nothing pure could be isolated. This was also the case for 2:1 reactions, which were performed in an effort to acquire bis-ligand complexes; in all cases intractable mixtures resulted.

The mass spectrum of compound **1** showed the molecular ion for the binuclear structure at 504 amu with an isotopic pattern that confirmed the composition  $\{([12]\text{-ane-P}_3\text{Et}_3)\text{Cu}_2\text{Cl}_2\}^+$ . In contrast, the bulkier  $^i\text{Pr}$  (**2**) and bromo (**3**) analogues gave rise to a highest ion in their mass spectra which does arise from the dissociation of  $\text{CuCl}_2$  (for **2**) or  $\text{CuBr}_2$  (for **3**) ( $\text{M}^+$  at  $m/z$  369). Thus the binuclear structure does appear to remain intact in the gas phase (and presumably also in solution) for **1**, but the bulkier  $[12]\text{-ane-P}_3\text{iPr}_3$  and bromo complexes show a greater tendency towards dissociation of the corresponding  $\text{CuX}_2^-$  anion. Solution conductivity measurements indicate the solutes to be only poor conductors in solution (in dichloromethane) which again suggests that the binuclear complexes are not extensively dissociated in this solvent. Although the isolated complexes showed no decomposition in air, they showed evidence of oxidative decomposition within hours when in solution. No  $\text{Cu}(\text{II})$  complexes were ever isolated, but the development of a green solution coloration (and ultimate precipitation from some solvents) upon continued exposure of solutions of the complexes to air did suggest the presence of  $\text{Cu}(\text{II})$ ; this was further supported by the loss of signal in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra as expected in the

presence of paramagnetic  $\text{Cu}(\text{II})$ .

## 60 Conclusion

The reactions of  $[12]\text{-ane-P}_3\text{R}_3$  with  $\text{Cu}(\text{I})$  halides lead to binuclear structures exhibiting a  $d^{10}\text{-}d^{10}$  closed shell ( $\text{Cu-Cu}$ ) interaction, or tetrahedral monomers depending upon the nature of the halide, and the substituent group on the phosphine donors. In all cases the macrocycle acts as a facially capping tridentate tris(phosphine) forming complexes with four coordinate tetrahedral geometries, or more heavily distorted five coordinate geometries with chloride and bromide mono bridging atoms. The macrocycle backbone has sufficient flexibility to favour pyramidal coordination *via* three mutually *cis* sites expanding the range of coordination environments and behaviour these macrocycles are capable of supporting.

## Experimental

**General information:** All reactions were carried out in an atmosphere of dry argon. All solvents were dried by boiling under reflux over standard drying agents. The compounds allylphosphine, *syn,syn*-1,5,9-triethyl-1,5,9-triphosphacyclododecane,  $[12]\text{-ane-P}_3\text{Et}_3$  were prepared by literature methods.<sup>2f</sup> All other reagents including Copper starting materials were obtained from the Aldrich Chemical Company. NMR spectra were recorded on a Bruker DPX-500 instrument at 500 MHz ( $^1\text{H}$ ), and 125.75MHz ( $^{13}\text{C}$ ), Bruker DPX-400 instrument at 400 MHz and 100 MHz ( $^{13}\text{C}$ ), Jeol Lamda Eclipse 300 at 121.65 MHz ( $^{31}\text{P}$ ), 75.57 MHz ( $^{13}\text{C}$ ).  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are quoted in ppm relative to residual solvent peaks, and  $^{31}\text{P}$  NMR chemical shifts quoted in ppm ( $\delta$ ) relative to 85% external  $\text{H}_3\text{PO}_4$  ( $\delta = 0\text{ppm}$ ). Mass spectra of all the samples have been measured by direct injection into a Waters Low Resolution ZQ Mass Spectrometer fitted with ESCI source, high resolution mass spectrometry (HRMS) was obtained on a Walters Q-tof mass spectrometer. Elemental analysis was performed by London Metropolitan University Analytical Service. In all cases the reactions are essentially quantitative, yields quoted are of recrystallised material.

## 95 Crystallography

Single-crystal XRD data for **3** and **4** were collected on an Agilent SupaNova Dual Atlas diffractometer with a mirror monochromator using either  $\text{Cu}$  ( $\lambda = 1.5418$  Å) radiation. Data for **1,2,5,6** and **7** data were collected on a Nonius Kappa CCD diffractometer using graphite monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71073$  Å). Sample temperature was maintained at 150K using an Oxford Cryosystems cooling apparatus. Crystal structures were solved and refined using SHELXS and refined using SHELXL.<sup>10</sup> Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were inserted in idealized positions, and a riding model was used with Uiso set at 1.2 or 1.5 times the value of  $U_{\text{eq}}$  for the atom to which they are bonded. One  $(\text{CH}_2)_3$  group of the ligand is disordered over two orientations in structures **1**, and **3**, with occupancies 0.72(1)/0.28(1) and 0.67(1)/ 0.33(1) respectively. All three groups are disordered in structure **7** with occupancies 0.52(2)/0.48(2), 0.566(2)/0.43(2), 0.74(1)/ 0.26(1). All disordered groups were refined with restrained geometry. The

isopropyl groups in **7** display elongated displacement parameters indicative of libration. All structure figures were drawn using Ortep3v2 for Windows, ellipsoids were drawn at 35% probability for all structures.<sup>11</sup> A summary of crystallographic data are available as ESI and the structures deposited with the Cambridge Structural Database (CCDC deposition numbers 1858168–1858174). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## 10 Syntheses

### [(12aneP<sub>3</sub>Et<sub>3</sub>)Cu(CuCl<sub>2</sub>)]**1**

To a solution of [12]-ane-P<sub>3</sub>Et<sub>3</sub> (150 mg, 0.49 mmol) dissolved in dichloromethane (15 ml) was added a suspension of CuCl (50 mg, 0.49 mmol) in dichloromethane (15 ml). The solution was stirred for 3 hrs during which time the copper chloride dissolved. The colourless solution was evaporated to dryness to give a white solid that was recrystallised by slow diffusion of 40/60 petroleum ether into a CH<sub>2</sub>Cl<sub>2</sub> solution of the residue to give **1** as white air-sensitive needles. Yield = 126 mg (49%), *Anal.*: found (calc.): C, 35.20 (35.72); H, 6.60 (6.59) %. MS(ES), *m/z*: 504.34 [46%, (M<sup>+</sup>)], <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ -29.9 ppm, <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.88 (br, m, 4H, PCH<sub>2</sub>CH<sub>2</sub>), 1.50 (br, m, 2H, PCH<sub>2</sub>CH<sub>2</sub>), 1.68 (br, m, 2H, PCH<sub>2</sub>CH<sub>3</sub>), 1.22 (br, m, PCH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 29.1 (br, PCH<sub>2</sub>), 22.1 (br, PCH<sub>2</sub>CH<sub>2</sub>), 20.9 (br, PCH<sub>2</sub>CH<sub>3</sub>), 8.1 (br, PCH<sub>2</sub>CH<sub>3</sub>).

### [(12aneP<sub>3</sub><sup>i</sup>Pr<sub>3</sub>)Cu(CuCl<sub>2</sub>)]**2**

Prepared as for **1**. Yield = 507 mg (46%), *Anal.*: found (calc.): C, 39.19 (39.56); H, 6.82 (7.19) %. MS(ES), *m/z*: 411.16 [100%, (M<sup>+</sup>-CuCl<sub>2</sub>)], HRMS: actual (calc.) mass: 411.1564 (411.1561) <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ -19.7 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.00 (br m, PCH<sub>2</sub>CH<sub>2</sub>), 1.70 (br m, PCH and PCH<sub>2</sub>), 1.10 (br m, CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ (ppm): 27.1 (br, PCH<sub>2</sub>), 24.9 (br, PCH<sub>2</sub>CH<sub>2</sub>), 21.4 (br, PCH), 17.8 (s, CH<sub>3</sub>) ppm.

### [(12aneP<sub>3</sub>Et<sub>3</sub>)Cu(CuBr<sub>2</sub>)]**3**

To a solution of [12]-ane-P<sub>3</sub>Et<sub>3</sub> (122 mg, 0.40 mmol) dissolved in dichloromethane (10 ml) was added CuBr (96 mg, 0.80 mmol) in dichloromethane (10 ml). The solution was stirred for 3 hrs during which time the copper bromide dissolved. The colourless solution was then evaporated to dryness to give a white solid that was recrystallised by slow diffusion of 40/60 petroleum ether into a CH<sub>2</sub>Cl<sub>2</sub> solution of the residue to give **3** as white air-sensitive needles. Yield = 96 mg (49%), *Anal.*: found (calc.): C, 30.22 (30.37); H, 5.43 (5.61) %. MS(ES), *m/z*: 369.1092 [100%, (M<sup>+</sup>)]. HRMS: actual (calc.) mass: 369.1092 (369.1091), <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ -28.1 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.85 (br m, PCH<sub>2</sub>), 1.58 (br m, PCH<sub>2</sub>CH<sub>2</sub>), 1.65 (br m, PCH<sub>2</sub>CH<sub>3</sub>), 1.16 (br m, PCH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 29.7 (br, PCH<sub>2</sub>), 21.4 (br, PCH<sub>2</sub>CH<sub>2</sub>), 22.3 (br, PCH<sub>2</sub>CH<sub>3</sub>), 8.54 (br, PCH<sub>2</sub>CH<sub>3</sub>) ppm.

### [(12aneP<sub>3</sub>Et<sub>3</sub>)CuBr]**4**

To a solution of [12]-ane-P<sub>3</sub>Et<sub>3</sub> (122 mg, 0.40 mmol) in

dichloromethane (10 ml) was added CuBr (48 mg, 0.40 mmol) in dichloromethane (10 ml) and the solution stirred for 3 hrs whereupon the copper bromide dissolved. The colourless solution was then evaporated to give a white solid which was recrystallised by slow diffusion of 40/60 petroleum ether into a CH<sub>2</sub>Cl<sub>2</sub> solution of the residue to give **4** as white air-sensitive needles. Yield = 94 mg (96%), *Anal.*: found (calc.): C, 40.01 (40.08); H, 7.29 (7.40) %. HRMS(ES), *m/z* (calc.) 369.1094 (369.1091) [100%, (M<sup>+</sup>)]. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ -28.7 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.93 (br m, PCH<sub>2</sub>), 1.61 (br m, PCH<sub>2</sub>CH<sub>2</sub>), 1.67 (br m, PCH<sub>2</sub>CH<sub>3</sub>), 1.10 (br m, PCH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 28.1 (br, PCH<sub>2</sub>), 21.8 (br, PCH<sub>2</sub>CH<sub>2</sub>), 20.5 (br, PCH<sub>2</sub>CH<sub>3</sub>), 8.50 (br, PCH<sub>2</sub>CH<sub>3</sub>) ppm.

### [(12aneP<sub>3</sub><sup>i</sup>Pr<sub>3</sub>)CuBr]**5**

Prepared as for **4** using [12]-ane-P<sub>3</sub><sup>i</sup>Pr<sub>3</sub>. Yield = 161 mg (94%), *Anal.*: found (calc.): C, 43.81 (43.95); H, 7.88 (7.99) %. HRMS(ES), *m/z* (calc.) 411.1556 (411.1561) [100%, (M<sup>+</sup>)]. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ -19.1 ppm, <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.90 (br m, PCH<sub>2</sub>CH<sub>2</sub>), 1.67 (br m, PCH and PCH<sub>2</sub>), 1.12 (br m, CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 28.1 (br, PCH<sub>2</sub>), 26.2 (br, PCH<sub>2</sub>CH<sub>2</sub>), 21.8 (br, PCH), 17.9 (s, CH<sub>3</sub>) ppm.

### [(12aneP<sub>3</sub>Et<sub>3</sub>)CuI]**6**

Prepared as for **4** but using CuI. Yield = 178 mg (98%), *Anal.*: found (calc.): C, 36.40 (36.26); H, 6.71 (6.69) %. HRMS(ES), *m/z* (calc.) 369.1103 (369.1091) [100%, (M<sup>+</sup>)]. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ -29.3 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.87 (br m, PCH<sub>2</sub>), 1.65 (br m, PCH<sub>2</sub>CH<sub>2</sub>), 1.67 (br m, PCH<sub>2</sub>CH<sub>3</sub>), 1.20 (br m, PCH<sub>2</sub>CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 28.4 (br, PCH<sub>2</sub>), 22.8 (br, PCH<sub>2</sub>CH<sub>2</sub>), 20.6 (br, PCH<sub>2</sub>CH<sub>3</sub>), 8.4 (br, PCH<sub>2</sub>CH<sub>3</sub>) ppm.

### [(12aneP<sub>3</sub><sup>i</sup>Pr<sub>3</sub>)CuI]**7**

Prepared as for **6** using [12]-ane-P<sub>3</sub><sup>i</sup>Pr<sub>3</sub>. Yield = 136 mg (91%), *Anal.*: found (calc.): C, 39.95 (40.12); H, 7.35 (7.29) %. HRMS(ES), *m/z* (calc.) 411.1569 (411.1561) [100%, (M<sup>+</sup>)]. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ -23.2 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.85 (br m, PCH<sub>2</sub>CH<sub>2</sub>), 1.60 (br m, PCH and PCH<sub>2</sub>), 1.13 (br m, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 28.4 (br, PCH<sub>2</sub>), 26.5 (br, PCH<sub>2</sub>CH<sub>2</sub>), 22.1 (br, PCH), 18.4 (s, CH<sub>3</sub>) ppm.

## Conflicts of Interest

There are no conflicts of interest to declare.

## Notes and references

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<sup>†</sup> Electronic Supplementary Information (ESI) available: Crystallographic details are provided in a single pdf file in the Supporting Information. The Supporting Information is available free of charge on the RSC Publications website.

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