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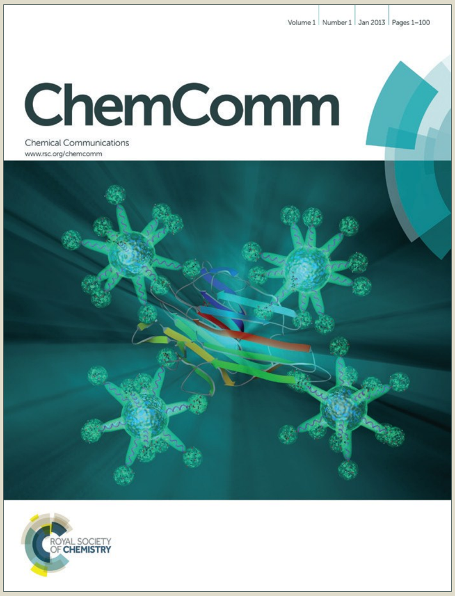

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Organometallic polyphosphorus and -arsenic ligands as linkers between pre-assembled linear Cu^I fragments

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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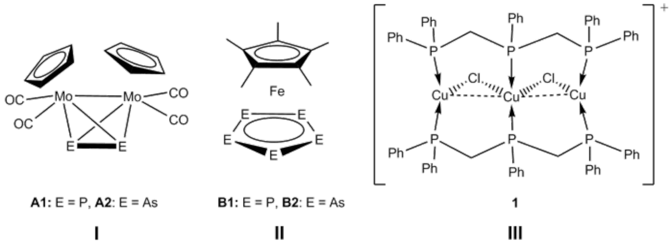
A simple and straightforward synthesis of a new linear trinuclear Cu^I cluster with polyphosphine ligands is presented. The reaction of this pre-organized Cu_3 precursor with E_n ligand complexes (E = P, As; n = 2, 5) affords discrete complexes exhibiting end-on η^1-coordination of the E_2 ligands or one-dimensional coordination polymers featuring σ-1,3-bridging E_5 rings, respectively.

In recent years, molecular wires have attracted increasing attention as promising nanostructured materials for molecular electronic, optical, and chemical devices.[1] Among these, homoleptic polymetallic linear arrays featuring multidentate bridging ligands and short intermetallic distances have been synthesized, bearing in some case conductive or semi-conductive behaviors.[2] Yet, the general access to such polymetallic molecular wires remains complicated as it is mostly hindered by the rather low structural control of the synthetic methods applied, which often led to polyhedral cluster cores instead of linear arrays. Therefore, there is interest to develop new synthetic approaches toward such polymetallic supramolecular arrays. The P_n organometallic ligand complexes **A1**, **B1** (scheme 1)[3,4] have been used previously as very versatile linking moieties between monovalent metal centers to afford spherical nano-sized supramolecular aggregates[5,6,7,8,9] as well as 1D and 2D coordination polymers.[10,11,12] However, these ligand complexes as well as their arsenic As_n analogs **A2**, **B2** (scheme 1)[13,14] have not yet been used to built-up extended molecular wires bearing polymetallic linear arrays with short metal-metal contacts. Herein we describe the reaction of E_n ligand complexes **A1**, **A2**, **B1** and **B2** (**A1**, **B1**: E = P; **A2**, **B2**: E = As, scheme 1) with a new trimetallic Cu^I linear precursor bearing short intermetallic distances to produce linear molecular wires. In a field where organic N, O or S donor ligands are the most commonly used linkers, this heteroleptic approach gives the opportunity to investigate: *i*) the effect of the variation of the nuclearity and geometry of the organometallic E_n ligand complexes on the dimension of the supramolecular entities formed; *ii*) the nature of the coordination modes adopted by the E_n ligands in such molecular assemblies; *iii*) how the variation of the pnictogen donor atom coordinated on Cu^I metal centers can alter intermetallic distances compared to the original linear trimetallic fragment.



Scheme 1. Representation of the molecular structures of the used E_n ligand complexes **A1**, **A2** and **B1**, **B2** as well as the newly synthesized trimetallic Cu^I entity **1** $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2]^+$.

A straightforward synthetic approach allowed us to obtain the new compound $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2][BF_4]$ (**1**) by self-assembly of 2 eq. of dpmp (dpmp = bis(diphenylphosphinomethyl)phenylphosphine), 2 eq. of CuCl and 1 eq. of $[Cu(CH_3CN)_4][BF_4]$ in CH_2Cl_2. Subsequent vapor diffusion of *n*-pentane into the crude solution afforded **1** as colorless crystals. The ^1H as well as the $^{31}P\{^1H\}$ NMR spectra of isolated crystals of compound **1** dissolved in CD_2Cl_2 suggest dynamic coordination behavior of the dpmp ligand coordinated on Cu^I metal centers at room temperature.[15]

The solid-state structure of **1** shows a $[Cu_3(\mu\text{-}Cl)_2(dpmp)_2]^+$ unit (fig. 1A), containing an almost linear trinuclear Cu^I fragment (Cu1-Cu2-Cu3; 159.5°) stabilized by two bridging η^1:η^1:η^1-dpmp ligands and two additional bridging Cl atoms. The Cu-Cu distances in **1** are short (2.8386(4) and 2.8782(4) Å) suggesting intramolecular metallophilic interactions. The terminal Cu^+ cations are coordinatively unsaturated and exhibit distorted trigonal planar geometries with the sum of the bond angles being 358.9° and 359.7°, respectively. Conversely, the internal Cu^I metal center has a distorted tetrahedral coordination sphere.

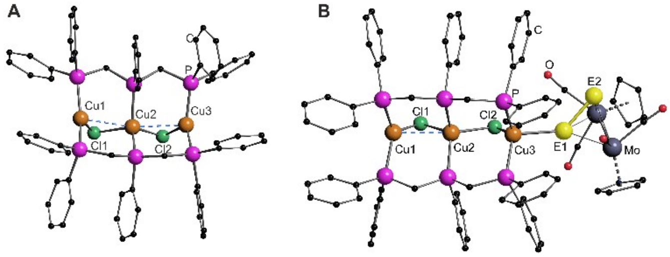


Fig. 1. Crystal structures of the complexes **1** (A) and the isostructural complexes **2** (E = P) and **3** (E = As) (B). The anion, hydrogen atoms and solvent molecules are omitted for clarity. Selected distances [Å] **1/2/3**: Cu1-Cu2 2.8782(4)/2.8359(7)/2.8304(8), Cu2-Cu3 2.8386(4)/3.3572(6)/3.2176(8), **2**: Cu3-P1 2.3693(10), P1–P2 2.0869(14), **3**: Cu3–As1 2.5295(7), As1-As2 2.3097(8).

A related [Cu_3] complex [$Cu_3(\mu\text{-}Cl)_2(dpmp)_2(MeCN)_2]^+[ClO_4]^-\cdot H_2O$ containing MeCN ligands coordinated to the terminal Cu^I metal centers (Cu1 and Cu3) was described previously, and shows larger intermetallic distances (ca. 3.2 Å).[16] This suggests that the terminal, trigonal planar Cu^I metal centers of **1** might be reactive and, therefore, compound **1** represents *a priori* an interesting linear [Cu_3] building block for supramolecular chemistry exhibiting close Cu···Cu contacts and potentially free, reactive, terminal coordination sites. Inspired by these observations, we intended to connect the [Cu_3] clusters of **1** by E_n ligand complexes **A1**, **A2**, **B1**, **B2** (scheme 1) (E = P, As). The addition of the tetrahedrane complexes **A1** or **A2** to a solution of **1** in CH_2Cl_2 affords clear red solutions of the products **2** and **3**, respectively. Vapor diffusion of *n*-pentane into CH_2Cl_2 solutions afforded orange (**2**) or dark red (**3**) crystals which can be isolated in good yields. Interestingly, the reported MeCN containing trinuclear Cu^I complex[16] does not react with E_n ligand complexes, what underlines the need of vacant coordination sites for a supramolecular aggregation. The ^1H NMR spectra of **2** and **3** show a set of signals for the dpmp ligands of the [Cu_3] unit very similar to those recorded for **1** and one singlet assignable to the Cp rings of **A1** or **A2**. The $^{31}P\{^1H\}$ NMR spectra of **2** and **3** show a set of signals for the [Cu_3] moiety slightly down field shifted compared to the signals registered for **1**. Additionally, **2** shows one singlet for the P_2 unit of **A1** at –65.6 ppm which is shifted 21 ppm upfield compared to the free ligand.[15] Single crystal X-ray diffraction analysis reveals isolated [$Cu_3(\mu\text{-}Cl)_2(dpmp)_2(\eta^1\text{-}L)]^+$ (L = **A1** (**2**), **A2** (**3**)) complexes (see figure 1B). The isostructural compounds **2** and **3** bear one tetrahedrane complex **A1** or **A2**, coordinated to one terminal, distorted tetrahedrally coordinated Cu^I atom of an almost linear [Cu_3] unit (Cu1-Cu2-Cu3; **2**: 164.81°; **3**: 164.72°). Therefore, the overall structure of the trimetallic core present in **1** is preserved upon these reactions. The other terminal Cu atom (Cu1 in figure 1B) exhibits a distorted trigonal planar geometry with the sum of angles being 358.6°(**2**) or 358.7°(**3**), respectively. The coordination environment of the central Cu^+ cation can best be described as distorted tetrahedral. The coordination of **A1** or **A2** as terminal ligands results in an elongation of the adjacent Cu···Cu distance inside the [Cu_3] chain while the E–E bond lengths of the coordinated E_2 ligands are almost unchanged compared to those of the free complexes (**2**: 2.0869(14) Å, **A1**: 2.079(2) Å[3]; **3**: 2.3097(8) Å, **A2**: 2.305(3) Å[13]). Therefore, the intermetallic distances Cu1–Cu2/Cu2–Cu3 are distinctly different with 2.8359(7) /3.3572(6) Å in **2** and 2.8304(8) /3.2176(8) Å in **3**, respectively. To investigate the influence of the coordination of the E_2 ligand complexes on the intermetallic distances found in the [Cu_3] cluster of **2** and **3**, DFT calculations on the model compound [$Cu_3(dmmp)_2(\mu\text{-}Cl)_2(\eta^1\text{-}$**A1**$)]^+$ (dmmp = bis(dimethylphosphino)-methylphosphane) were performed.[17] The results show that the closer ligand **A1** approaches the Cu3 atom, the longer the Cu2–Cu3 distance gets (labeling according to figure 1B). In contrast, the Cu1–Cu2 distance is unaffected by the coordination of **A1** to Cu3 and can be very well compared with the starting compound **1**. The solid state structures of **2** and **3** show that the elongation of the Cu2···Cu3 distance is more pronounced in the case of the P_2 ligand **A1** instead of the As_2 ligand **A2**. Supporting this observation, the calculated dissociation energies of the E_n ligand in [$Cu_3(\mu\text{-}Cl)_2(dpmp)_2(\eta^1\text{-}L)]^+$ (L = **A1**(**2**): 36.5 kJ·mol^{-1}, **A2**(**3**) 31.7 kJ·mol^{-1}) are slightly higher for L = **A1** (**2**) suggesting a stronger interaction of the P_2 fragment with the [Cu_3] unit.

As a next step, we focused our attention on the use of the sandwich complexes [$Cp^*Fe(\eta^5\text{-}E_5)$] (E = P (**B1**), As(**B2**)). The addition of complexes **B1** or **B2** to **1** in CH_2Cl_2 afforded a clear green solution of the product **4** and a clear brown solution of derivative **5**, respectively. Vapor diffusion of *n*-pentane into CH_2Cl_2 solutions afforded light green (**4**) or brown (**5**) crystals as needles. The ^1H NMR spectra of **4** and **5** in CD_2Cl_2 show in addition to the set of signals for the dpmp ligands one singlet assignable to the Cp* rings of **B1** or **B2** at a similar chemical shift compared to the free complexes. The $^{31}P\{^1H\}$ NMR spectra of the derivatives **4** and **5** in CD_2Cl_2 show a set of signals for the dpmp ligands of the [Cu_3] cluster slightly down field shifted compared to the signals observed for compound **1**. Only one singlet for the *cyclo*-P_5 ligand **B1** at 149.9 ppm is detected, which is shifted 3 ppm upfield compared to the free ligand.[4] Single crystal X-ray diffraction analysis reveals that **4** and **5** are isostructural and consist of a one-dimensional coordination polymer of almost linear [Cu_3] units (Cu1-Cu2-Cu3; **4**: 168.78°; **5**: 169.12°) connected by *cyclo*-E_5 complexes (see figure 2) with the general formula [$Cu_3(dpmp)_2(\mu\text{-}Cl)_2\{\mu\text{-}L\}]_n[BF_4]_n$ (L = **B1** (**4**), **B2** (**5**)).

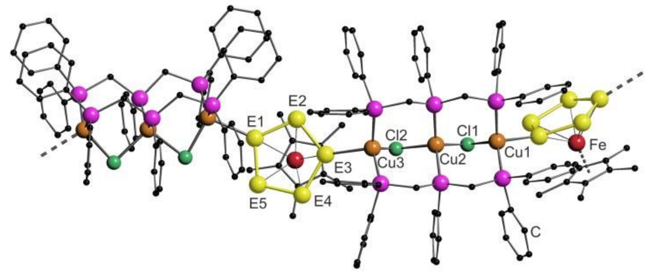


Fig. 2. Section of the structures of the isostructural coordination polymers **4** (E = P) and **5** (E = As). The anion, hydrogen atoms and solvent molecules are omitted for clarity. Selected distances **4/5** [Å]: Cu1-Cu2 3.2975(8)/3.2135(8), Cu2-Cu3 3.3389(8)/3.0345(8), Cu1-E1 2.3743(11)/2.5036(7), Cu3-E3 2.3271(10)/2.5980(8).

The *cyclo*-E_5 ligands **B1** and **B2** are bridging two Cu centers in a σ-1,3-coordination mode. This σ-coordination mode is unprecedented for the *cyclo*-As_5 ligand **B2**. For the phosphorus compound **B1** the 1,3-coordination mode was only observed towards coordination with $Cr(CO)_5$ and CuI.[12,18] The intermetallic distances Cu1–Cu2 /Cu2–Cu3 are different with 3.2975(8)/3.3389(8) Å in **4** and 3.2135(8)/3.0345(8) Å in **5**, revealing shorter Cu–Cu distances for the As_5 ligand complex **B2** as organometallic linker. The E–E bond lengths of the *cyclo*-E_5 ligands in both compounds are very uniform. The calculated energies for the dissociation of **B1** and **B2** for the monomeric complexes [$Cu_3(dpmp)_2(\mu\text{-}Cl)_2\{\eta^1\text{-}L\}]^+$ (L = **B1**, **B2**) of 41.2 kJ·mol^{-1} (**4**) and 31.9 kJ·mol^{-1} (**5**) are relatively low which is in agreement with the observed dynamic coordination behavior of the complexes in solution.[15] We previously described a preferred η^2-coordination mode of the [$Cp^*Fe(\eta^5\text{-}As_5)$] ligand **B2** towards Cu^I cations.[19] The fact that **B2** exhibits a σ-coordination mode is probably caused by steric repulsion of the phenyl substituents of the dpmp ligand and the Cp* ligand. According to DFT calculations, a η^2-coordination of **B2** to the [Cu_3] cluster is disfavored by 17.0 kJ·mol^{-1}.[17]

In conclusion, a simple route to prepare the cationic building block $[Cu_3(dpmp)_2(\mu\text{-}Cl)_2]^+$ (**1**) is presented. The $[Cu_3]$ cluster **1** features two vacant coordination sites, which allows the reaction with the E_2 and E_5 ligand complexes resulting in the isolation of discrete complexes **2** and **3** and one-dimensional coordination polymers **4** and **5**, respectively. Surprisingly, the polyphosphorus and –arsenic complexes show the same η^1-coordination of the E_2 ligands **A1** and **A2**, and even more astonishing, the same and rarely observed bridging σ-1,3-coordination of the E_5 ligands which is so far unprecedented for the *cyclo*-As_5 complex **B2**. The intermetallic Cu···Cu distances of the $[Cu_3]$ cluster are dependent on the strength of the coordination to the terminal Cu atoms. The stronger the E-Cu coordination, the longer the adjacent Cu–Cu distance.

This study demonstrates the preparation of easily accessible extended metal atom chains and exemplifies the potential of E_n ligand complexes as connecting moieties resulting from their adjustable bonding modes. The solubility and dynamic coordination behavior of the isolated compounds show the features of the $[Cu_3]$ cluster **1** as well as the E_n ligand complexes to act as building blocks in supramolecular chemistry. These observations will likely allow for a large variety of new supramolecular assemblies in the future.

Acknowledgments: The work was supported by the Deutsche Forschungsgemeinschaft. C. L. thanks the Alexander von Humboldt Foundation for a fellowship of experienced researcher.

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Notes and references

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† Details of all X-ray structure analysis can be found in the supplementary information. CCDC-1038416-1038421.

Electronic Supplementary Information (ESI) available: Experimental, theoretical, analytical and crystallographic details. See DOI: 10.1039/c000000x/

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