

## Coordination Chemistry

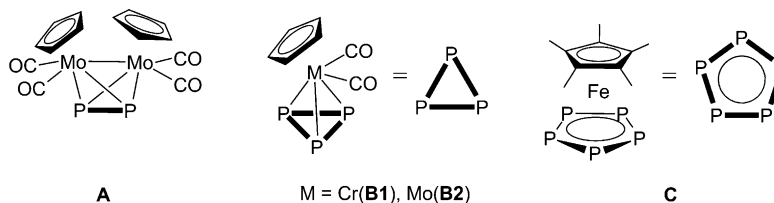
Highly Dynamic Coordination Behavior of  $P_n$  Ligand Complexes towards “Naked”  $\text{Cu}^+$  CationsMartin Fleischmann,<sup>[a]</sup> Stefan Welsch,<sup>[a]</sup> Eugenia V. Peresyphkina,<sup>[b, c]</sup> Alexander V. Virovets,<sup>[b, c]</sup> and Manfred Scheer\*<sup>[a]</sup>

Dedicated to Professor Kenton H. Whitmire on the occasion of his 60th birthday

**Abstract:** Reactions of  $\text{Cu}^+$  containing the weakly coordinating anion  $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$  with the polyphosphorus complexes  $[\{\text{CpMo}(\text{CO})_2\}_2(\mu, \eta^2: \eta^2\text{-P}_2)]$  (**A**),  $[\text{CpM}(\text{CO})_2(\eta^3\text{-P}_3)]$  ( $\text{M} = \text{Cr}$  (**B1**),  $\text{Mo}$  (**B2**)), and  $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$  (**C**) are presented. The X-ray structures of the products revealed mononuclear (**4**) and dinuclear (**1**, **2**, **3**)  $\text{Cu}^I$  complexes, as well as the one-dimensional coordination polymer (**5a**) containing an unprecedented  $[\text{Cu}_2(\text{C}_3)]^{2+}$  paddle-wheel building block. All products are readily soluble in  $\text{CH}_2\text{Cl}_2$  and exhibit fast dynamic coordination behavior in solution indicated by variable temperature  $^{31}\text{P}\{\text{H}\}$  NMR spectroscopy.

spheres or capsules with a fullerene-like construction of five- and six-membered rings.<sup>[4]</sup> Reactions of  $P_n$  ligand complexes with salts of metal cations  $\text{M}^+$  ( $\text{M} = \text{Cu}$ ,  $\text{Ag}$ ,  $\text{Au}$ ) containing small anions, such as halides,  $[\text{BF}_4]^-$ , or  $[\text{PF}_6]^-$ , tend to result in almost insoluble products, which complicates further characterization of the products. In the meantime, the use of the weakly coordinating anion (WCA)  $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$  ([TEF]) allowed the isolation of coordination compounds including  $P_n$  ligand complexes and the monocations  $\text{Ag}^+$ ,<sup>[5]</sup>  $\text{Ga}^+$ ,<sup>[6]</sup>  $\text{In}^{+}$ <sup>[7]</sup> and  $\text{Ti}^+$ ,<sup>[8]</sup> which have good solubility even in  $\text{CH}_2\text{Cl}_2$  and show a highly dynamic behavior in solution. Recently, a synthesis for the  $\text{Cu}^+$  salt  $[\text{Cu}(\text{o-DFB})_2][\text{TEF}]$  ( $\text{o-DFB} = \text{ortho-difluorobenzene}$ ) was published by Krossing and co-workers.<sup>[9]</sup> Intrigued by the fact that this “naked”  $\text{Cu}^+$  cation enabled the coordination of

Supramolecular coordination chemistry of multidentate linker molecules connecting metal centers has become an established field of research during the last decades.<sup>[1]</sup> Next to a large variety of extended metal organic frameworks (MOFs), prominent examples also include molecular cycles, spheres, and cubes.<sup>[2]</sup> Our group contributed to this field in particular by the use of  $P_n$  ligand complexes as linkers. These organometallic linker complexes possess substituent-free P atoms, which can donate to multiple metal atoms in a variety of bonding modes.<sup>[3]</sup> This flexible coordination ability afforded a large number of unique coordination compounds in the last years. The most prominent examples represent “inorganic fullerenes” consisting of  $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$  (Scheme 1 C) and  $\text{Cu}^I$  halides, which represent



**Scheme 1.** Representation of the  $P_n$  ligand complexes ( $n = 2, 3$ , and  $5$ ) reacted with  $[\text{Cu}(\text{o-DFB})_2][\text{TEF}]$ .

the weakly nucleophilic ligands, elemental sulfur ( $\text{S}_8$ )<sup>[9]</sup> and white phosphorus ( $\text{P}_4$ ),<sup>[10]</sup> we strived to investigate the reactivity of this new  $\text{Cu}^+$  source towards  $P_n$  ligand complexes under these weakly coordinating conditions. We expect that the higher Lewis acidity of  $\text{Cu}^+$  will have an impact on the observed arrangements and facilitate different coordination modes of the  $P_n$  complexes compared to former studies including  $\text{Ag}^+$  and  $\text{Ti}^+$ . The latter showed mainly formation of coordination polymers with *cyclo-P*<sub>3</sub> or *cyclo-P*<sub>5</sub> ligand complexes.<sup>[5–7]</sup>

Herein, we describe the reactions of  $[\text{Cu}(\text{o-DFB})_2][\text{TEF}]$  with selected  $P_n$  ligand complexes containing two, three, and five P atoms (Scheme 1)<sup>[11]</sup> and the full characterization of the resulting products. Among other new structural motifs, an unprecedented paddle-wheel building block was found in addition to molecular units that have previously been proposed as intermediates for aggregation in  $\text{Ag}^+$  chemistry.

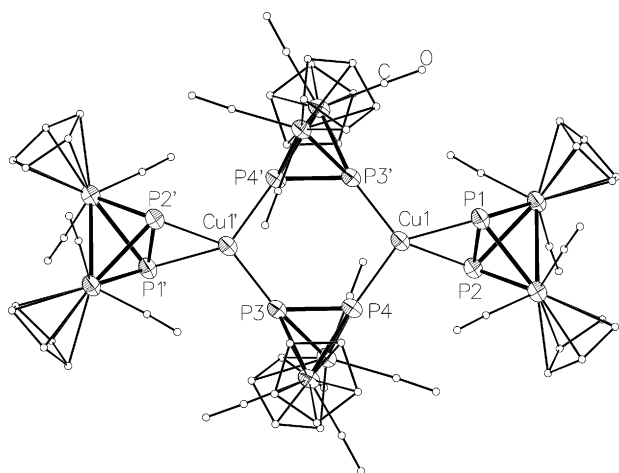
It is noteworthy that the isolated yields from all described reactions are generally between good and excellent (ca. 50–85%).<sup>[12]</sup> When the  $\text{Cu}^+$  source  $[\text{Cu}(\text{o-DFB})_2][\text{TEF}]$  was reacted

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201502775>.



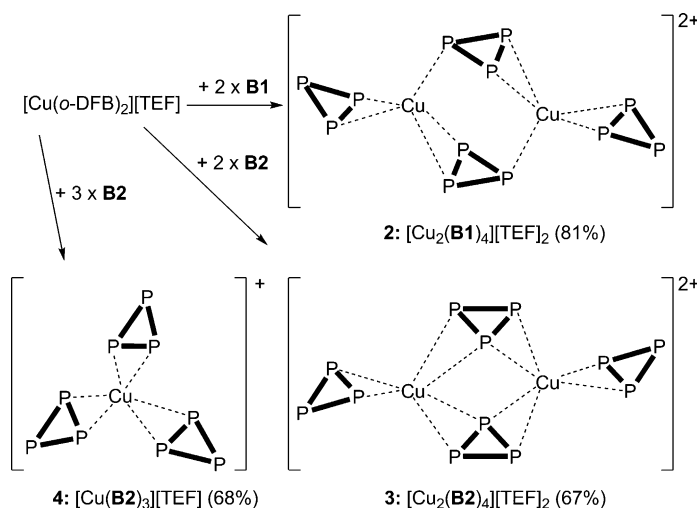
**Figure 1.** Illustration of the dicationic complex of the solid-state structure of compound **1**. Ellipsoids are drawn at 50% probability. H atoms are omitted for clarity. Selected bond lengths [Å]: Cu1–P1 2.359(3), Cu1–P2 2.368(3), Cu1–P4 2.277(2), Cu1–P3' 2.240(3), P1–P2 2.164(3), P3–P4 2.088(3), P1–Cu1–P2 54.48(8).

with the  $P_2$  ligand **A**, compound **1** was isolated in 58% yield. Single-crystal X-ray structural analysis of the red crystals revealed a dinuclear  $Cu^I$  complex with a central  $M_2P_4$  ( $M=Cu$ ) six-membered ring (Figure 1). This structural motif was previously observed for  $Cu^+$ ,  $Ag^+$ ,  $Au^+$  and  $Tl^+$ .<sup>[8,13,14]</sup> The side-on coordinated P–P bonds are elongated (2.164(3) Å) compared with the  $\eta^1:\eta^1$ -bridging P–P bonds with 2.088(3) Å. The Cu–P distances to the bridging ligands are shorter (ca. 2.25 Å) than to the terminal ligands (ca. 2.36 Å). The folding angle of the six-membered ring measures 6.8(1)°, which is smaller compared with the analogues Cu complexes with  $[BF_4]^-$  or  $[PF_6]^-$  anions. The  $^{31}P\{^1H\}$  NMR spectrum in  $CD_2Cl_2$  solution points to dynamic coordination behavior and shows only one singlet shifted upfield by 40 ppm compared to the free ligand **A**. The  $^1H$ ,  $^{13}C\{^1H\}$ , and  $^{19}F$  NMR spectra show characteristic signals for the CO and Cp ligands, as well as for the [TEF] anion, respectively. In the ESI mass spectra from a  $CH_2Cl_2$  solution, a peak assignable to the monocation  $[Cu(A)_2]^+$  as a half of the isolated molecule was found.

When  $[Cu(o-DFB)_2][TEF]$  was reacted with the *cyclo*- $P_3$  complexes **B1** and **B2**, the three different coordination compounds **2–4** were isolated (see Scheme 2). The reaction of the  $CrP_3$  complex **B1** with  $[Cu(o-DFB)_2][TEF]$  led to the isolation of the dinuclear complex  $[Cu_2(B1)_4]^{2+}$  (**2**) regardless of the used stoichiometry of the reactants. In contrast, reactions of the  $MoP_3$  complex **B2** with  $[Cu(o-DFB)_2][TEF]$  initially led to a mixture of two products. One of these is the dinuclear complex  $[Cu_2(B2)_4]^{2+}$  (**3**), whereas the other is the mononuclear Cu complex  $[Cu(B2)_3]^+$  (**4**) bearing three ligands of **B2**. By tuning the stoichiometry with an excess of the  $Cu^+$  salt or the ligand **B2**, we were also able to isolate the compounds **3** and **4** as the only products, respectively.

The solid-state structures of **2** and **3** (Figures 2 and 3) revealed a similar assembly of two  $Cu^+$  cations bound to a terminal  $\eta^2$ -coordinated  $P_3$  ligand and two bridging ones. Although **B1** coordinates the two Cu atoms in **2** in a  $\mu,\eta^1:\eta^2$ -mode, **B2** binds in a  $\mu,\eta^2:\eta^2$ -mode. In both cases, all side-on coordinated P–P bonds are elongated compared to the free ligands, whereas the rest is not significantly changed.

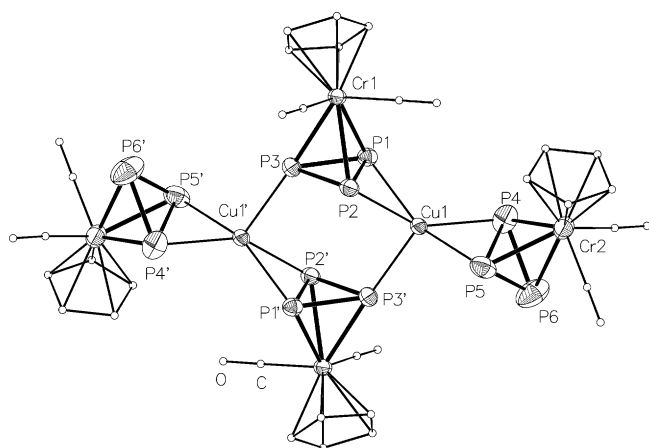
Compound **4** crystallizes in the trigonal space group  $P\bar{3}$  as a molecular monomeric cationic complex with two independent Cu atoms on the threefold axis, each coordinated side-on by one P–P bond of three  $MoP_3$  ligands **B2** (Figure 4b). Figure 4a illustrates the trigonal planar geometry of one coordination unit, while Figure 4c shows the staggered arrangement to the next unit along the crystallographic *c* axis. The intermolecular distances in **4** are far too long for any additional Cu–P interactions. This solid-state structure consistently shows an elongation of the  $\eta^2$ -coordinated P–P bonds. It is noteworthy that similar reactions with the *cyclo*- $P_3$  ligands **B1** and **B2** with  $In^+$ ,  $Tl^+$  and  $Ag^+$  always lead to the formation of one-dimensional polymers instead of discrete monomeric or dimeric complexes, such as compounds **2–4**.<sup>[5b,7b]</sup>



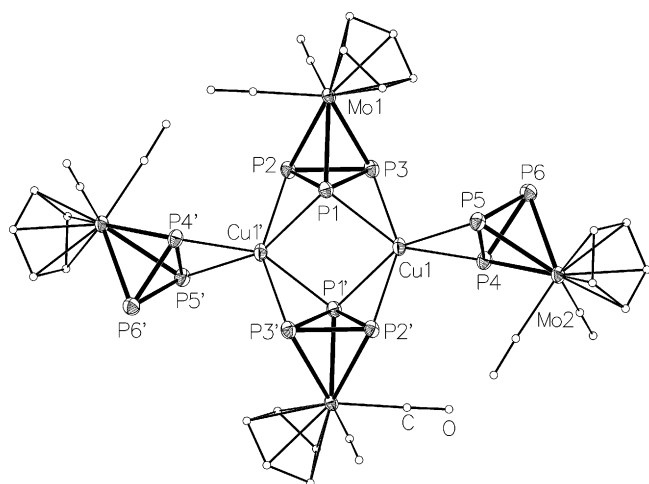
**Scheme 2.** Reaction Scheme of  $Cu^+$  and the *cyclo*- $P_3$  ligands (see Scheme 1) **B1** ( $M=Cr$ ) and **B2** ( $M=Mo$ ) illustrating their bonding modes in the compounds **2–4**.

The structures of **2–4** resemble the species postulated as intermediates of the equilibrium involving the *cyclo*- $P_3$  ligand **B2** and  $Ag^+$  in solution calculated by DFT methods.<sup>[5b]</sup> Therefore, the structures may be viewed as snapshots of the species in solution. The bridging  $\eta^2:\eta^2$ -coordination mode found in **3** has never been observed for a *cyclo*- $P_3$  complex before, but for a *cyclo*- $As_3$  complex in the product obtained from the reaction of  $Ag[TEF]$  and  $[Cp^*Mo(CO)_2(\eta^3-As_3)]$ .<sup>[15]</sup> Clearly, the higher Lewis acidity of the  $Cu^+$  cation provokes the *cyclo*- $P_3$  complex **B2** to bind in a  $\pi$ -coordination mode analogues to the *cyclo*- $As_3$  ligand complex.

The *cyclo*- $P_3$  containing compounds **2–4** are readily soluble in  $CD_2Cl_2$ , and their  $^1H$ ,  $^{13}C\{^1H\}$ , and  $^{19}F$  NMR spectra showed the characteristic signals for CO and Cp ligands and the [TEF]



**Figure 2.** Solid-state structure of the dication of compound **2**. Ellipsoids are drawn at 50% probability. H atoms are omitted for clarity. Selected bond lengths [Å]: Cu1–P1 2.414(1), Cu1–P2 2.463(1), Cu1–P3' 2.450(1), Cu1–P4 2.375(2), Cu1–P5 2.363(2), P1–P2 2.227(2), P2–P3 2.129(2), P1–P3 2.139(2), P4–P5 2.254(2), P5–P6 2.129(2), P4–P6 2.119(2).



**Figure 3.** Solid-state structure of the dication of compound **3**. Ellipsoids are drawn at 50% probability. H atoms are omitted for clarity. Selected bond lengths [Å]: Cu1–P1 2.487(1), Cu1–P2 2.469(1), Cu1–P3' 2.456(1), Cu1–P4 2.385(1), Cu1–P5 2.403(1), P1–P2 2.225(1), P2–P3 2.141(1), P1–P3 2.246(1), P4–P5 2.249(1), P5–P6 2.163(1), P4–P6 2.127(1).

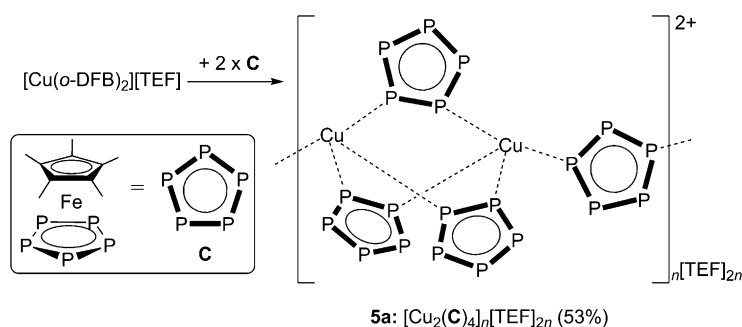
anion, respectively. Their  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra recorded at room temperature each revealed one singlet at  $\delta = -288.4$  ppm (**2**),  $-339.9$  ppm (**3**), and  $-342.4$  ppm (**4**). Although this signal is not shifted compared to the free ligand **B1** ( $\delta = -288.3$  ppm) in **2**, it is shifted upfield for the ligand **B2** ( $-351.9$  ppm) in **3** and **4**. Upon cooling the samples, first, a significant broadening of the signal was observed, and finally the signal split into two singlets at 183 K ( $-309.3$ ,  $-231.5$  ppm for **2** and  $-363.3$ ,  $-283.6$  ppm for **3**) in a 2:1 ratio.<sup>[16]</sup> Our explanation of this behavior in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra involves a dissociation of the dicationic  $[\text{Cu}_2(\text{L})_4]^{2+}$  species into monocationic  $[\text{Cu}(\text{L})_2]^+$  ( $\text{L} = \text{B1}, \text{B2}$ ) complexes in solution.<sup>[17,18]</sup> This

signal splitting is most probably caused by a hindered rotation of side-on coordinated  $\text{P}_3$  ligands of the species  $[\text{Cu}(\text{L})_2]^+$  at low temperature.

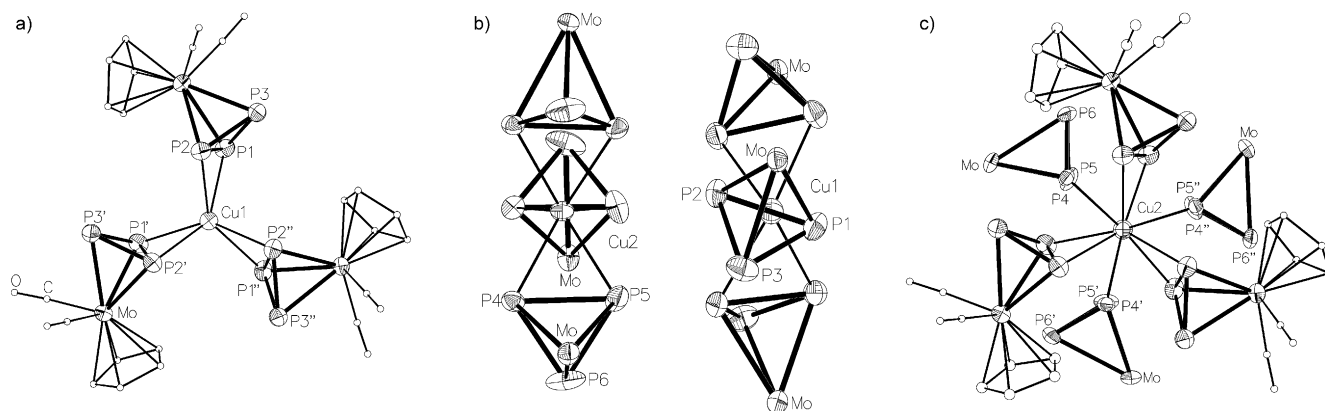
Since we reported the first examples of the coordination chemistry of the pentaphosphaferrocene complex  $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$  (**C**) with  $\text{Cu}^{\text{I}}$  and terminally bound halides,<sup>[4]</sup> we were always interested to investigate its chemistry towards free  $\text{Cu}^+$ . Unfortunately, the combination of **C** and  $[\text{Cu}(\text{MeCN})_4][\text{X}]$  ( $\text{X} = \text{BF}_4, \text{PF}_6$ ) always resulted in the formation of insoluble brown precipitates. When **C** was reacted with  $[\text{Cu}(\text{o-DFB})_2][\text{TEF}]$ , the formation of a clear brown solution was observed (Scheme 3). From these reactions, brown rod-shaped crystals of **5a** were obtained.

The single-crystal X-ray structural analysis of **5a** revealed a one-dimensional coordination polymer with an unprecedented paddle-wheel repeating unit  $[\text{Cu}_2(\text{C})_3]^{2+}$  interconnected by a  $\sigma$ -1,3-bridging *cyclo-P*<sub>5</sub> ligand **C**. Caused by disorder of the [TEF] anions, we encountered severe problems refining the crystal structure of **5a**. Therefore, we exchanged the anion [TEF] for another WCA [FAl] ( $= [\text{FAl}\{\text{OC}_6\text{F}_{10}(\text{C}_6\text{F}_5)_3\}_3]^-$ ) to obtain the analogous one-dimensional coordination polymer  $[\text{Cu}_2(\text{C})_4]_n[\text{FAl}]_{2n}$  (**5b**) as single-crystals of appropriate quality.<sup>[19]</sup> The crystal structure of **5b** is shown in Figure 5. Although three *cyclo-P*<sub>5</sub> ligands **C** bridge two Cu atoms in a  $\sigma$ -1,2-coordination mode to form a trigonal paddle-wheel, one additional  $\text{P}_5$  ligand **C** connects these paddle-wheels through a  $\sigma$ -1,3-bridging coordination. The resulting Cu–P bonds showed a lengths distribution in the range between 2.298(2) and 2.435(2) Å, whereas all P–P bonds revealed uniform lengths from 2.089(3) to 2.118(4) Å.

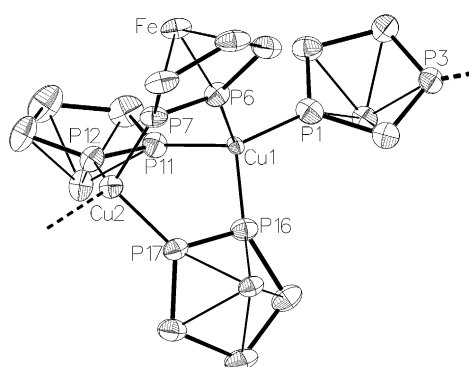
Compound **5a** is readily soluble in  $\text{CD}_2\text{Cl}_2$ , and the  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{19}\text{F}$  NMR spectra consistently showed only characteristic signals for the Cp\* ligands and the anion [TEF]. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum recorded at room temperature showed a singlet at  $\delta = 142.7$  ppm shifted upfield compared to free **C** (152.2 ppm). Upon cooling, the singlet broadens significantly below 273 K and finally splits into at least three very broad signals ( $\delta \approx 100, 120, 140$  ppm).<sup>[16]</sup> Coupling of P–P or Cu–P could not be resolved. This behavior is indicative of dynamic coordination including equilibrium between monomeric  $[\text{Cu}(\text{C})_2]^+$  and dimeric  $[\text{Cu}_2(\text{C})_4]^{2+}$  species, which were also observed for  $\text{Ag}^+$ .<sup>[5a]</sup>



**Scheme 3.** Reaction of  $\text{Cu}^+$  with the *cyclo-P*<sub>5</sub> ligand **C** giving the one-dimensional coordination polymer **5a**.



**Figure 4.** Section of the solid-state structure of **4**; viewing directions along (a and c) or perpendicular (b) to the crystallographic *c* axis. Ellipsoids are drawn at 50% probability. H atoms and anions are omitted for clarity. a) One independent trigonal coordination unit. b) Packing of two consecutive trigonal coordination units represented by the central heavy atoms only for clarity. c) Staggered configuration of the independent trigonal units. The second unit (labeled) is only represented by the heavy atoms. Cu2 in front of Cu1; P5 hidden by P4; Selected bond lengths [Å]: Cu1–P1 2.434(2), Cu1–P2 2.427(3), Cu2–P4 2.432(2), Cu2–P5 2.422(3), P1–P2 2.244(3), P2–P3 2.132(3), P1–P3 2.146(3), P4–P5 2.239(3), P5–P6 2.148(3), P4–P6 2.131(3).



**Figure 5.** Illustration of the cationic repeating unit of the coordination polymer **5b**. Ellipsoids are drawn at 50% probability. Cp\* ligands are omitted for clarity. Selected bond lengths [Å]: Cu1–P1 2.300(3), Cu1–P6 2.435(2), Cu1–P11 2.374(3), Cu1–P16 2.406(2), Cu2–P3 2.256(3), Cu2–P7 2.302(3), Cu2–P12 2.298(2), Cu2–P17 2.336(2).

Our results demonstrate the facile preparation of the new Cu<sup>I</sup> complexes **1–5b** featuring the WCAs [TEF] and [FAI] and selected P<sub>*n*</sub> ligand complexes. In contrast to earlier reported Cu<sup>I</sup> halide derivatives, all products reported herein show a good solubility even in weakly donating solvents, such as CH<sub>2</sub>Cl<sub>2</sub>, which enables their characterization in solution. <sup>31</sup>P{<sup>1</sup>H} NMR solution studies revealed highly dynamic coordination behavior. The X-ray structures of the Cu<sup>+</sup> products **2–4** differ significantly from the former reported Ag<sup>+</sup> complexes. The *cyclo*-P<sub>3</sub> ligands form dinuclear (**2**, **3**) or mononuclear (**4**) complexes with Cu<sup>+</sup> instead of one-dimensional coordination polymers for Ag<sup>+</sup>. Therefore, the newly isolated assemblies of Cu<sup>+</sup> can be viewed as snapshots of the species in solution postulated by DFT calculations for previously investigated Ag<sup>+</sup> complexes containing *cyclo*-P<sub>3</sub> ligands. Therefore, they can be viewed as transient species of the Ag<sup>+</sup> chemistry. Moreover, the bonding mode of the *cyclo*-P<sub>3</sub> ligand is changed in the dicationic complexes [Cu<sub>2</sub>(L)<sub>4</sub>]<sup>2+</sup> (L = **B1**(**2**), **B2**(**3**)) when exchanging

the central metal atom of the ligand from Cr to Mo. The reaction of the *cyclo*-P<sub>5</sub> ligand complex **C** and Cu<sup>+</sup> gave a coordination polymer featuring an unprecedented dicationic [Cu<sub>2</sub>(C)<sub>3</sub>]<sup>2+</sup> paddle-wheel-shaped building block. Finally, the presented class of soluble Cu<sup>I</sup> compounds featuring P<sub>*n*</sub> ligand complexes will help to understand ligand-exchange equilibrium in solution, which is not possible for the poorly soluble Cu<sup>I</sup> halide analogues. The described complexes will further serve as suitable supramolecular building blocks for the formation of organometallic–organic hybrid materials by the introduction of additional linker molecules.

## Acknowledgements

This work was comprehensively supported by the Deutsche Forschungsgemeinschaft. S.W. thanks the Fonds der Chemischen Industrie for a PhD fellowship. The COST action CM1302 SIPs is gratefully acknowledged. The authors thank Prof. Dr. Ruth Gschwind and Dr. Matthias Fleischmann for DOSY NMR measurements and Dr. Christian Gröger for MAS NMR measurements.

**Keywords:** coordination chemistry · copper · dynamics · polyphosphorus complexes · weakly coordinating anions

- [1] a) R. W. Saalfrank, A. Scheurer, *Top. Curr. Chem.* **2012**, *319*, 125–170; b) J.-M. Lehn, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4763–4768; c) N. Lanigan, X. Wang, *Chem. Commun.* **2013**, *49*, 8133–8144.
- [2] a) L. F. Lindoy, K.-M. Park, S. S. Lee, *Chem. Soc. Rev.* **2013**, *42*, 1713–1727; b) N. J. Young, B. P. Hay, *Chem. Commun.* **2013**, *49*, 1354–1379.
- [3] a) B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* **2010**, *110*, 4164–4177; b) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.* **2010**, *110*, 4178–4235; c) O. J. Scherer, *Acc. Chem. Res.* **1999**, *32*, 751–762.
- [4] a) J. Bai, A. V. Virovets, M. Scheer, *Science* **2003**, *300*, 781–783; b) M. Scheer, A. Schindler, C. Gröger, A. V. Virovets, E. V. Peresypkina, *Angew. Chem. Int. Ed.* **2009**, *48*, 5046–5049; *Angew. Chem.* **2009**, *121*, 5148–5151; c) M. Scheer, A. Schindler, J. Bai, B. P. Johnson, R. Merkle, R. Winter, A. V. Virovets, E. V. Peresypkina, V. A. Blatov, M. Sierka, H. Eckert, *Chem.*

- Eur. J.* **2010**, *16*, 2092–2107; d) S. Welsch, C. Gröger, M. Sierka, M. Scheer, *Angew. Chem. Int. Ed.* **2011**, *50*, 1435–1438; *Angew. Chem.* **2011**, *123*, 1471–1474.
- [5] a) M. Scheer, L. J. Gregoriades, A. V. Virovets, W. Kunz, R. Neueder, I. Krossing, *Angew. Chem. Int. Ed.* **2006**, *45*, 5689–5693; *Angew. Chem.* **2006**, *118*, 5818–5822; b) L. J. Gregoriades, B. K. Wegley, M. Sierka, E. Brunner, C. Gröger, E. V. Peresypkina, A. V. Virovets, M. Zabel, M. Scheer, *Chem. Asian J.* **2009**, *4*, 1578–1587.
- [6] M. Fleischmann, S. Welsch, H. Krauss, M. Schmidt, M. Bodensteiner, E. V. Peresypkina, M. Sierka, C. Gröger, M. Scheer, *Chem. Eur. J.* **2014**, *20*, 3759–3768.
- [7] a) S. Welsch, M. Bodensteiner, M. Dušek, M. Sierka, M. Scheer, *Chem. Eur. J.* **2010**, *16*, 13041–13045; b) M. Fleischmann, S. Welsch, L. J. Gregoriades, C. Gröger, M. Scheer, *Z. Naturforsch. B* **2014**, *69*, 1348–1356.
- [8] S. Welsch, L. J. Gregoriades, M. Sierka, M. Zabel, A. V. Virovets, M. Scheer, *Angew. Chem. Int. Ed.* **2007**, *46*, 9323–9326; *Angew. Chem.* **2007**, *119*, 9483–9487.
- [9] G. Santiso-Quiñones, A. Higelin, J. Schaefer, R. Brückner, C. Knapp, I. Krossing, *Chem. Eur. J.* **2009**, *15*, 6663–6677.
- [10] G. Santiso-Quiñones, A. Reisinger, J. Slattery, I. Krossing, *Chem. Commun.* **2007**, 5046–5048.
- [11] a) O. J. Scherer, H. Sitzmann, G. Wolmershäuser, *J. Organomet. Chem.* **1984**, *268*, C9–C12; b) L. Y. Goh, R. C. S. Wong, O. J. Scherer, A. Schneider in *Inorganic Synthesis*, Wiley, Hoboken, **2007**, pp. 247–250; c) O. J. Scherer, H. Sitzmann, G. Wolmershäuser, *Acta Crystallogr. Sect. C* **1985**, *41*, 1761–1763; d) O. J. Scherer, T. Brück, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 59–61; *Angew. Chem.* **1987**, *99*, 59–61.
- [12] See the Supporting Information for details.
- [13] M. Scheer, L. J. Gregoriades, M. Zabel, J. Bai, I. Krossing, G. Brunklaus, H. Eckert, *Chem. Eur. J.* **2008**, *14*, 282–295.
- [14] The related compound with [BF<sub>4</sub>]<sup>−</sup> is described in the Supporting Information.
- [15] L. J. Gregoriades, H. Krauss, J. Wachter, A. V. Virovets, M. Sierka, M. Scheer, *Angew. Chem. Int. Ed.* **2006**, *45*, 4189–4192; *Angew. Chem.* **2006**, *118*, 4295–4298.
- [16] Representation of the spectra can be found in the Supporting Information.
- [17] We assume a highly dynamic coordination behavior that cannot be resolved on the NMR timescale at room temperature. Furthermore, it was supported by DOSY NMR measurements and DFT calculations for related Ag<sup>+</sup> compounds (see the Supporting Information).
- [18] This assumption is based on the similar behavior of the related Ag<sup>+</sup> compounds, see Ref. [5 b].
- [19] Direct synthesis of a suitable Cu<sup>+</sup> source featuring the WCA [FAI] failed after several attempts. The synthesis of **5b** involves a mixed Li<sup>+</sup>/Tl<sup>+</sup> salt and is described in the Supporting Information.

Received: July 15, 2015

Published online on August 20, 2015