

# Highly soluble Cu(I)-acetonitrile salts as building blocks for novel phosphorus-rich organometallic-inorganic compounds

Mehdi Elsayed Moussa,<sup>‡</sup> Martin Piesch,<sup>‡</sup> Martin Fleischmann,<sup>‡</sup> Andrea Schreiner,<sup>‡</sup> Michael Seidl<sup>‡</sup> and Manfred Scheer<sup>\*a</sup>

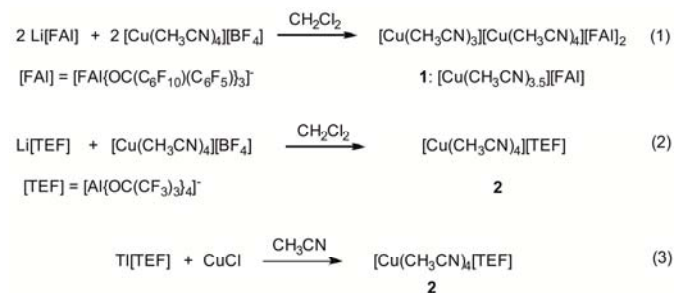
The synthesis of the air-stable and highly soluble Cu(I)-acetonitrile salts  $[\text{Cu}(\text{CH}_3\text{CN})_{3.5}][\text{FAL}]$  (**1**) ( $[\text{FAL}] = \text{FAL}\{\text{OC}(\text{C}_6\text{F}_{10})(\text{C}_6\text{F}_5)\}_3$ ) and  $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{TEF}]$  (**2**) ( $[\text{TEF}] = \text{Al}\{\text{OC}(\text{CF}_3)_3\}_4$ ) is presented. Compound **1** reacts with the organometallic polyphosphorus complexes  $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$  (**A**) and  $[(\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5))]$  (**B**) and salt **2** reacts with **B** to form one new (**3**) and three unprecedented (**4-6**) phosphorus-rich Cu(I) dimers with the general formulas  $[\text{Cu}_2(\mu, \eta^1:\eta^1\text{-A})_2(\eta^2\text{-A})_2][\text{FAL}]_2$  (**3**),  $[\text{Cu}_2(\mu, \eta^1:\eta^1\text{-A})_2(\eta^1\text{-CH}_3\text{CN})_4][\text{FAL}]_2$  (**4**),  $[\text{Cu}_2(\mu, \eta^1:\eta^1\text{-B})_2(\eta^1\text{-CH}_3\text{CN})_4][\text{FAL}]_2$  (**5**) and  $[\text{Cu}_2(\mu, \eta^1:\eta^1\text{-B})_2(\eta^1\text{-CH}_3\text{CN})_4][\text{TEF}]_2$  (**6**).

In recent years, the number of Cu(I) complexes stabilized by polydentate ligands has increased rapidly owing to their rich coordination chemistry and wide range of applications.<sup>1</sup> The majority of these ligands possess N or P donor atoms,<sup>2</sup> while fewer possess S, O and other donor atoms.<sup>3</sup> Among the very useful, and somehow air-stable, starting materials for the synthesis of these Cu(I) complexes are salts such as tetrakis(acetonitrile) Cu(I),  $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{X}]$  ( $[\text{X}] = [\text{BF}_4]^-$ ,  $[\text{PF}_6]^-$ ,  $[\text{ClO}_4]^-$ ,  $[\text{SbF}_6]^-$ ).<sup>4</sup> However, due to the usually limited solubility of the aforementioned salts, there is an increasing interest in the use of better soluble Cu(I) sources as starting materials.<sup>5</sup> One key concept for the synthesis of such compounds is to employ bulky, weakly coordinating anions (WCAs). For example, a synthesis of the Cu(I) salts  $[\text{Cu}(1,2\text{-F}_2\text{C}_6\text{H}_4)_2][\text{TEF}]$  and  $[\text{Cu}(\text{CH}_2\text{Cl}_2)_2][\text{TEF}]$  ( $[\text{TEF}] = [\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ ) was published by Krossing and co-workers.<sup>5b</sup> These salts do not only show good solubility in  $\text{CH}_2\text{Cl}_2$ , but were also used as starting materials to form original compounds such as the first example of arene- and cyclo sulfur complexes of Cu(I). Thus, stable, highly soluble and easily (on a multi-gram scale) accessible Cu(I) salts are in urgent demand to allow the expansion of the Cu(I) chemistry to new fields of materials science.

One active research area of our group focuses on the study of the coordination chemistry of substituent-free

polyphosphorus ( $\text{P}_n$ ) ligand complexes.<sup>6</sup> These organometallic compounds show flexible coordination behaviours and can be used as connectors between metal ions affording a large number of coordination polymers (CPs) and fullerene-like inorganic nanospheres.<sup>7</sup> Moreover, recent studies focused on three-component reactions of such  $\text{P}_n$  ligand complexes with metal salts and organic molecules yielding unprecedented hybrid CPs.<sup>8</sup> However, reactions of these  $\text{P}_n$  building blocks with salts of metal cations containing small anions, such as halides,  $[\text{BF}_4]^-$  and  $[\text{PF}_6]^-$  resulted in products of limited solubility, which complicated their further characterisation in solution.<sup>7g,h,8a,c</sup>

Accordingly, we targeted the design of Cu(I) salts with bulky WCAs to increase their solubility and with coordinated acetonitrile ligands to increase their air-stability. Herein, we present the synthesis of the highly soluble and air-stable compounds  $[\text{Cu}(\text{CH}_3\text{CN})_{3.5}][\text{FAL}]$  (**1**) ( $[\text{FAL}] = [\text{FAL}\{\text{OC}(\text{C}_6\text{F}_{10})(\text{C}_6\text{F}_5)\}_3]$ ) and  $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{TEF}]$  (**2**) and show their use as building blocks for unprecedented  $\text{P}_n$ -based organometallic-inorganic complexes. The reaction of the Cu(I) salt **1** with  $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$  (**A**) afforded the dimers  $[\text{Cu}_2(\mu, \eta^1:\eta^1\text{-A})_2(\eta^2\text{-A})_2][\text{FAL}]_2$  (**3**) and  $[\text{Cu}_2(\mu, \eta^1:\eta^1\text{-A})_2(\eta^1\text{-$



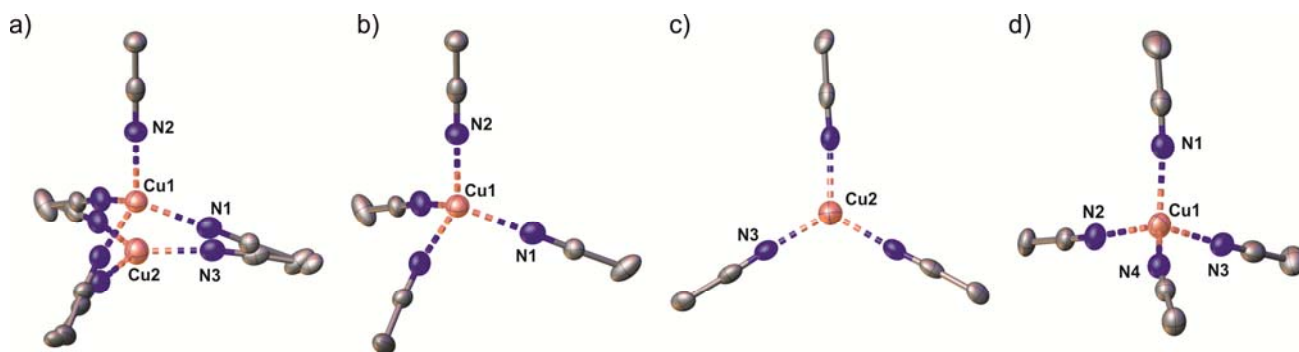
**Scheme 1.** Metathesis reactions affording: (1)  $[\text{Cu}(\text{CH}_3\text{CN})_{3.5}][\text{FAL}]$  (**1**) with alternating  $[\text{Cu}(\text{CH}_3\text{CN})_3]^+$  and  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  complex cations and (2,3)  $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{TEF}]$  (**2**).

<sup>a</sup> Institut für Anorganische Chemie der Universität Regensburg, 93040 Regensburg, Germany. E-mail: manfred.scheer@chemie.uni-r.de

<sup>†</sup> Dedicated to Prof. Helmut Sitzmann on the occasion of his 60<sup>th</sup> birthday.

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<sup>‡</sup>These authors contributed equally to this work.



**Figure 1.** Cationic parts in the crystal structures of: a-c)  $[\text{Cu}(\text{CH}_3\text{CN})_{3.5}][\text{FAI}]$  (**1**) and d)  $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{TEF}]$  (**2**). a) Superposition of the tetrahedral  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  and the trigonal planar  $[\text{Cu}(\text{CH}_3\text{CN})_3]^+$  complex cations. b) Coordination environment of Cu1. c) Coordination environment of Cu2. Ellipsoids are drawn at 50% probability. H atoms are omitted for clarity.

$\text{CH}_3\text{CN})_4][\text{FAI}]_2$  (**4**), respectively, depending on the ratio of **A**:**1** used in the reaction. Moreover, salts **1** and **2** react with  $[(\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5))]$  (**B**) to form the dimers  $[\text{Cu}_2(\mu, \eta^1:\eta^1\text{-B})_2(\eta^1\text{-CH}_3\text{CN})_4][\text{FAI}]_2$  (**5**) and  $[\text{Cu}_2(\mu, \eta^1:\eta^1\text{-B})_2(\eta^1\text{-CH}_3\text{CN})_4][\text{TEF}]_2$  (**6**) respectively. Although the coordination chemistry of  $\text{P}_n$  ligand complexes towards metal salts were studied in the past, the heteroleptic dimers **4-6** are unprecedented in this field.

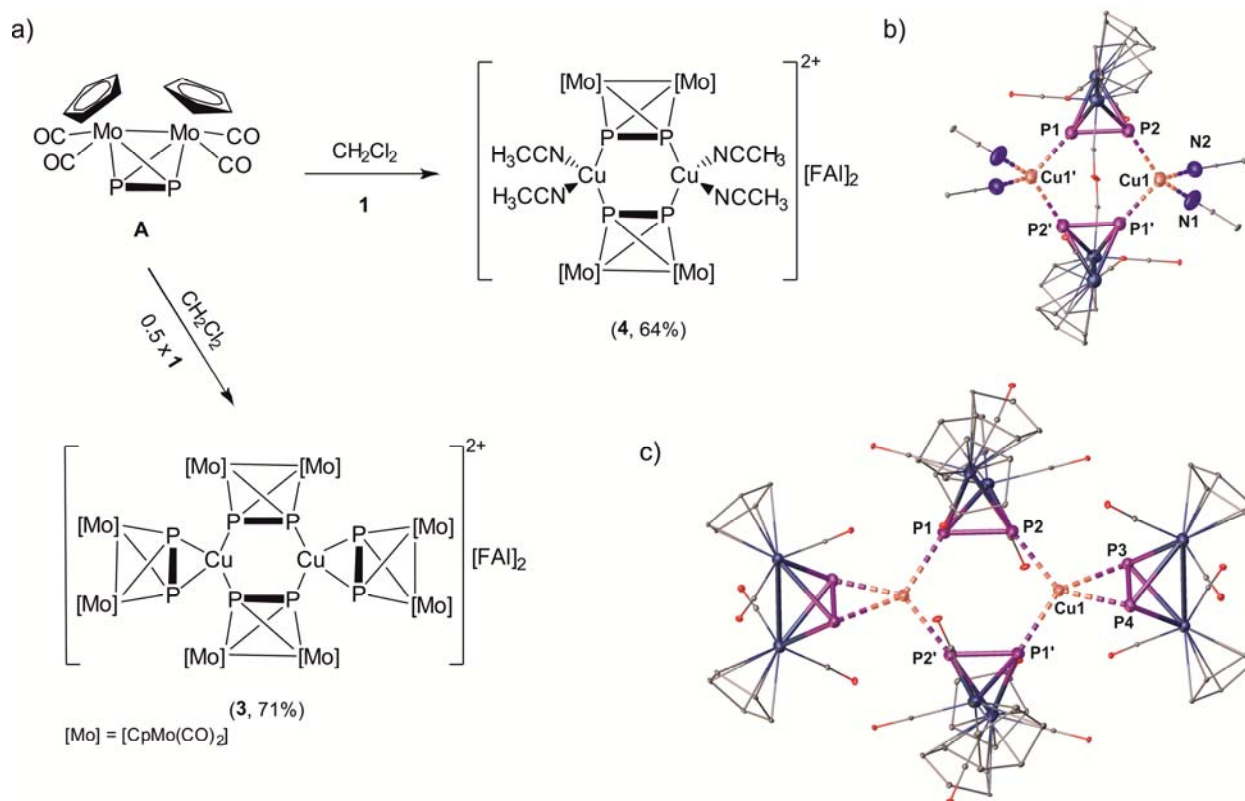
The Cu(I) salts  $[\text{Cu}(\text{CH}_3\text{CN})_{3.5}][\text{FAI}]$  (**1**) and  $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{TEF}]$  (**2**) can be obtained by sonicating the corresponding lithium salt of the WCA with  $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{BF}_4]$  in  $\text{CH}_2\text{Cl}_2$ . Moreover, (**2**) can be prepared by a room temperature metathesis reaction between  $\text{Ti}[\text{TEF}]$  and  $\text{CuCl}$  in  $\text{CH}_3\text{CN}$  (Scheme 1). Both compounds **1** and **2** are highly soluble in common organic solvents such as  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CN}$ , THF, ethyl acetate and ethanol but insoluble in alkanes. Surprisingly, they also show good solubility in low-dielectric solvents such as toluene and ethyl ether. Moreover, solids of **1** and **2** are air-stable and can be handled and weighed on the benchtop. This was confirmed by elemental analyses of the solids after 24 hours storage on air, which were identical to the measurements of the initially handled samples. Single crystals of **1** and **2** were obtained by layering  $\text{CH}_2\text{Cl}_2$  or  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  solutions of **1** and **2**, respectively, with *n*-hexane (Figure 1). Compound **1** crystallizes in the trigonal space group P-3, while **2** crystallizes in the non-centrosymmetric space group  $\text{P}2_12_12_1$  of the orthorhombic crystal system. The cationic part in the crystal structure of **1** reveals two close Cu(I) positions (50:50 ratio, Figure 1a), which are both situated directly on the threefold rotational axis. The two Cu(I) atoms exhibit either a trigonal planar coordination with three  $\text{CH}_3\text{CN}$  ligands or a tetrahedral coordination with four  $\text{CH}_3\text{CN}$  ligands. Therefore, the Cu(I) salt **1** contains the  $[\text{Cu}(\text{CH}_3\text{CN})_3]^+$  and  $[\text{Cu}(\text{CH}_3\text{CN})_4]^+$  cations in equimolar ratio in an alternating sequence along the crystallographic *c*-axis. This composition is also confirmed by elemental analysis. The cationic part in the crystal structure of **2** shows one Cu(I) atom adopting a tetrahedral coordination environment to which four  $\text{CH}_3\text{CN}$  ligands (Figure 1d) are

coordinated. The Cu-N (1.941(6)-2.012(4) Å) and C-N (1.128(5)-1.226 Å) bond lengths in **1** and **2** are comparable and slightly elongated compared to those observed in the known tetrahedral Cu(I) complex  $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{ClO}_4]$  (Cu-N = 1.99 Å average, C-N = 1.10(2)-1.14(2) Å).<sup>9</sup>

The room temperature  $^1\text{H}$  NMR spectra of **1** and **2** in  $\text{CD}_2\text{Cl}_2$  reveal single signals (**1** ( $\delta$  = 2.20 ppm), **2** ( $\delta$  = 2.18 ppm)) attributed to the  $\text{CH}_3\text{CN}$  ligands rendering them, in both compounds, all equivalent on the NMR timescale. The  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of **1** shows a set of signals for the  $[\text{FAI}]$  anion, while it reveals for **2** a single signal at ca. -75.6 ppm attributed to the  $[\text{TEF}]$  anion. In the ESI-MS from  $\text{CH}_2\text{Cl}_2$  solutions of **1** and **2**, only peaks assignable to the cations  $[\text{Cu}(\text{CH}_3\text{CN})_n]^+$  ( $n = 2, 3, 4$ ) and the anions  $[\text{TEF}]$  or  $[\text{FAI}]$  are observed (cf. ESI).

Previous studies by our group show that the ligand complex  $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$  (**A**) reacts with Cu(I) salts to give exclusively dimers of the general formula  $[\text{Cu}_2(\mu, \eta^1:\eta^1\text{-A})_2(\eta^2\text{-A})_2][\text{X}]_2$  ( $[\text{X}] = [\text{BF}_4]^-$ ,  $[\text{PF}_6]^-$ ,  $[\text{TEF}]^-$ ).<sup>5a,10</sup> Moreover, we reported recently the formation of the 1D CPs  $[\text{Cu}_2(\text{B})_4]_n[\text{X}]_{2n}$  ( $[\text{X}] = [\text{FAI}]^-$ ,  $[\text{TEF}]^-$ ) from the reaction of  $[(\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5))]$  (**B**) with  $[\text{Cu}(\text{o-DFB})_2][\text{TEF}]$  or its reaction with  $[\text{Ti}(\text{CH}_2\text{Cl}_2)_x][\text{Li}(\text{FAI})_2]$  and  $\text{CuCl}$ .<sup>5a</sup> In this work, the isolation of the new Cu(I) salts **1** and **2** raised the question about the possibility to use them in further Cu(I) chemistry. Due to their enhanced solubility, their reactions with polyphosphorus ligand complexes can probably allow the formation of new, unprecedented coordination compounds.

In a first step, the  $\text{P}_2$  ligand complex **A** was reacted with the Cu(I) salt **1** in  $\text{CH}_2\text{Cl}_2$  at room temperature (Figure 2a). This reaction afforded selectively the products **3** (71% yield) or **4** (64% yield) depending on the ratio of **A**:**1** used, (2:1 ratio, **3**) and (1:1 ratio, **4**). Compounds **3** and **4** crystallize at room temperature from *n*-pentane diffusion into the solutions of the crude reaction mixtures; their structures were examined by X-ray crystallography (cf. Figure 2b,c and ESI). In each case, the crystal structures reveal a dinuclear



**Figure 2.** a) Reaction of  $[\text{Cu}(\text{CH}_3\text{CN})_5][\text{FAI}]$  (**1**) with  $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$  (**A**). Crystal structure of the dinuclear complex cation in, b) **4** and c) **3**. Ellipsoids are drawn at 50% probability. C atoms are drawn as small spheres and H atoms are omitted for clarity.

$\text{Cu}(\text{I})$  complex for which each  $\text{Cu}(\text{I})$  atom is coordinated by two  $\text{P}_2$  ligands **A** in a  $\eta^1:\eta^1$  coordination mode. Thus, a central, almost planar,  $\text{Cu}_2\text{P}_4$  six-membered ring is observed for both **3** and **4** (Figure 2b,c). The coordination spheres of the  $\text{Cu}(\text{I})$  centers in **3** are each completed by two other P atoms from one side-on coordinated  $\text{P}_2$  ligand complex **A**. This structural motif was previously observed for  $\text{Cu}(\text{I})$ ,  $\text{Ag}(\text{I})$ ,  $\text{Au}(\text{I})$ , and  $\text{Tl}(\text{I})$ .<sup>5a,10,11</sup> In contrast, each of the coordination spheres of the  $\text{Cu}(\text{I})$  centers in **4** are completed by two N atoms from two coordinated  $\text{CH}_3\text{CN}$  ligands. This renders **4** a unique coordination compound in the supramolecular chemistry of the  $\text{P}_2$  ligand complex **A** ready for subsequent reactions. The P-P and Cu-P bond lengths in **3** and **4** range between 2.2571(9)-2.3335(9) and 2.0760(10)-2.1509(11) Å, respectively. These values are comparable to those reported for assemblies built from the  $\text{P}_2$  ligand complex **A** and  $\text{Cu}(\text{I})$  salts.<sup>5a,10</sup>

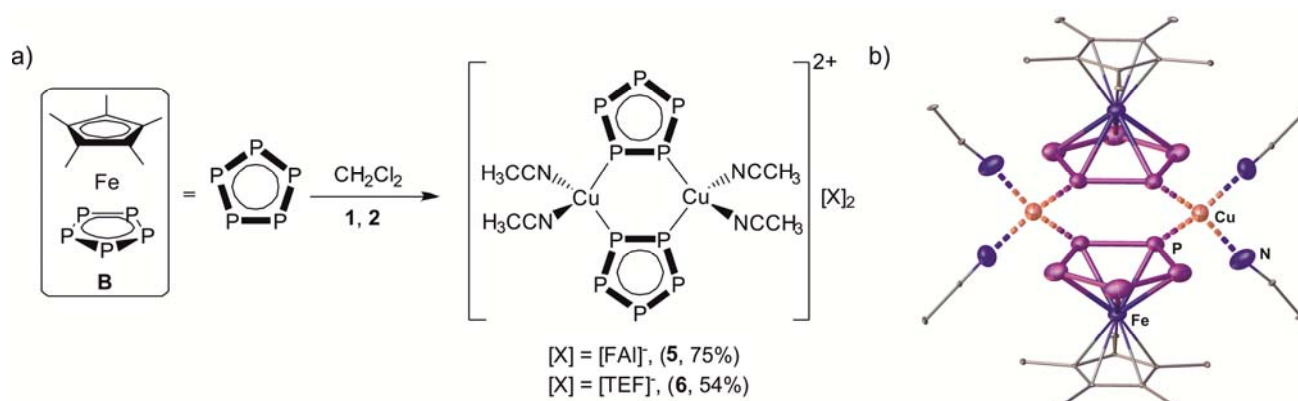
The compounds **3** and **4** are readily soluble in  $\text{CH}_3\text{CN}$ ,  $\text{CH}_2\text{Cl}_2$  and THF. They show poor solubility in toluene and are insoluble in alkanes. Their room temperature  $^{31}\text{P}\{\text{H}\}$  NMR spectra in  $\text{CD}_2\text{Cl}_2$  exhibit single signals at -84.7 and -82.5 ppm, respectively, which are shifted by about 40-43 ppm upfield compared to uncoordinated **A**

(-43.0 ppm).<sup>10</sup> Their room temperature  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}\{\text{H}\}$  NMR spectra show typical signals for the Cp and CO ligands of the  $\text{P}_2$  moieties as well as for the  $[\text{FAI}]^-$  anion. In the ESI mass spectrum of **3** in  $\text{CH}_2\text{Cl}_2$ , only one signal for the  $[\text{Cu}(\text{A})_2]^+$  cation is observed while signals attributed to the monocations  $[\text{Cu}(\text{A})_2(\text{CH}_3\text{CN})]^+$  and  $[\text{Cu}(\text{A})_2]^+$  are detected in that of **4**. These NMR and ESI-MS data reveal a partial dissociation instead of a full dissociation of the assemblies **3** and **4** in solutions of  $\text{CH}_2\text{Cl}_2$ .

A similar reaction of complex **A** with the  $\text{Cu}(\text{I})$  salt **2**, afforded a product with the general formula  $[\text{Cu}_2(\mu, \eta^1:\eta^1\text{-A})_2(\eta^2\text{-A})_2][\text{TEF}]_2$ . The solid state structure of this compound shows a cationic part very similar to that of the dimer **3**. The same compound was previously reported by us using the  $\text{Cu}^{\text{I}}$  salt  $[\text{Cu}(\text{o-DFB})_2][\text{TEF}]$  (o-DFB = ortho-difluorobenzene).<sup>5a</sup>

The partial substitution of the  $\text{CH}_3\text{CN}$  ligands in the  $\text{Cu}(\text{I})$  source **1** by the complex **A** leading to the unprecedented heteroleptic dinuclear complex **4** motivated us to expand our study to the *cyclo*- $\text{P}_5$  ligand complex  $[(\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5))] (\text{B})$ .

When **B** is reacted with **1** or **2** in a 1:1 stoichiometry in  $\text{CH}_2\text{Cl}_2$ , light green crystals of the compounds **5** or **6** could be selectively



**Figure 3.** a) Reaction of  $[\text{Cu}(\text{CH}_3\text{CN})_{3.5}][\text{FAI}]$  (**1**) and  $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{TEF}]$  (**2**) with  $(\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5))$  (**B**). b) Crystal structure of the dinuclear complex cation in **5** (**6** have a similar structure). Ellipsoids are drawn at 50% probability. C atoms are drawn as small spheres and H atoms are omitted for clarity.

obtained upon layering the crude reaction mixtures with *n*-hexane (Figure 3). These compounds are isolated in good to high yields and are air- and light-stable in the solid state. Similar reactions using a 2:1 or 3:1 ratio of **B**:(**1** or **2**) exclusively yielded the products **5** and **6**, which contain a 1:1 ratio of **B**:**1** or **2**. Single crystal X-ray diffraction analyses of **5** and **6** reveal in each case a dinuclear  $[\text{Cu}_2(\mu, \eta^1: \eta^1\text{-B})_2(\text{CH}_3\text{CN})_4]^{2+}$  complex cation (Figure 3). The structure shows an almost perfectly planar central  $\text{Cu}_2\text{P}_4$  six-membered ring, which is a frequently observed structural motif in the supramolecular coordination compounds including the complex **B** and  $\text{Cu}^{\text{I}}$  halides.<sup>7f,g,12</sup> The  $[\text{Cp}^*\text{Fe}]$  complex fragments point to opposite sides of the  $\text{Cu}_2\text{P}_4$  plane. The tetrahedral coordination environment of each Cu atom is additionally completed by two labile  $\text{CH}_3\text{CN}$  ligands. The Cu-P bonds lengths in **5** and **6** are in the range between 2.2778(5) and 2.2803(5) Å, which are comparable to those observed in the previously reported 1D CPs obtained from **B** and  $\text{Cu}(\text{I})$  salts of  $[\text{FAI}]^-$  and  $[\text{TEF}]^-$ .<sup>5a</sup> The C-N distances in **5** and **6** range between 1.130(2) and 1.141(7) Å and are similar to those observed in the  $\text{Cu}(\text{I})$  salts **1** and **2**.

Compounds **5** and **6** are readily soluble in  $\text{CH}_3\text{CN}$  or in a 1:1 mixture of  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$ , well soluble in  $\text{CH}_2\text{Cl}_2$  but insoluble in alkanes. Their room temperature  $^1\text{H}$  NMR spectra in  $\text{CD}_2\text{Cl}_2$  solution show in each case one singlet at ca.  $\delta = 2.00$  ppm attributed to the  $\text{CH}_3\text{CN}$  ligands and one singlet at ca.  $\delta = 1.40$  ppm for the  $\text{Cp}^*$  ligand of complex **B**. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra exhibit, in each case, only one singlet ( $\{\delta = 147.0$  ppm, **5**},  $\{\delta = 138.9$  ppm, **6**}, which is upfield shifted compared to that reported for the free complex **B** ( $\delta = 152.2$  ppm).<sup>13</sup> This suggests a dynamic coordination in  $\text{CH}_2\text{Cl}_2$  solutions of **5** and **6** comparable to those of the previously described coordination compounds of  $\text{Cu}(\text{I})$  towards polyphosphorus ligand complexes.<sup>5a</sup> The  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of **5** shows a characteristic set of signals for the  $[\text{FAI}]^-$  anion while that of **6** displays a singlet centered at ca.  $\delta = -78.10$  ppm assigned to the  $[\text{TEF}]^-$  anion. ESI-MS spectra from  $\text{CH}_2\text{Cl}_2$  solutions of **5** and **6** show peaks assignable to the monocationic complexes  $[\text{Cu}(\text{B})_2(\text{CH}_3\text{CN})]^+$ ,  $[\text{Cu}(\text{B})(\text{CH}_3\text{CN})]^+$  and  $[\text{Cu}(\text{B})_2]^+$ . The NMR and ESI-MS data of both compounds reveal only a partial dissociation of the formed assemblies in  $\text{CH}_2\text{Cl}_2$  solutions. Elemental analyses of the crystals show that these compounds do not lose the  $\text{CH}_3\text{CN}$  ligands upon drying in vacuum.

The reason why not all the  $\text{CH}_3\text{CN}$  ligands of the  $\text{Cu}(\text{I})$  sources **1** and **2** were substituted by the *cyclo*- $\text{P}_5$  complex **B** is not clear. It is probably attributable to steric effects arising from the bulkiness of

the complex **B**. Nevertheless, this partial substitution results in the formation of the heteroleptic dinuclear complexes **5** and **6**, which are unprecedented in the coordination chemistry of the  $\text{P}_5$  ligand complex. In addition, the presence of the terminal labile  $\text{CH}_3\text{CN}$  ligands in these dimers make them valuable building blocks for further supramolecular aggregation reactions. It is worth to note that previous attempts to react the ligand complex **B** with  $\text{Cu}(\text{CH}_3\text{CN})_4[\text{BF}_4]^-$  or  $\text{Cu}(\text{CH}_3\text{CN})_4[\text{PF}_6]^-$  resulted solely in unstructurally characterised products.<sup>14</sup> This emphasizes the high need of soluble  $\text{Cu}^{\text{I}}$  precursors such as **1** and **2** in supramolecular synthesis.

## Conclusions

In conclusion, we have presented the synthesis of two novel  $\text{Cu}(\text{I})$ -acetonitrile salts,  $[\text{Cu}(\text{CH}_3\text{CN})_{3.5}][\text{FAI}]$  (**1**) and  $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{TEF}]$  (**2**), which reveal air-stability and high solubility in common organic solvents. The  $\text{Cu}(\text{I})$  salt **1** was reacted with the  $\text{P}_n$  ligand complexes  $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\eta^2\text{-P}_2)]$  (**A**) and  $(\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5))$  (**B**) to give the new homoleptic  $[\text{Cu}_2(\mu, \eta^1: \eta^1\text{-A})_2(\eta^2\text{-A})_2][\text{FAI}]_2$  (**3**) and unprecedented heteroleptic  $[\text{Cu}_2(\eta^1: \eta^1\text{-A})_2(\eta^1\text{-CH}_3\text{CN})_4][\text{FAI}]_2$  (**4**) and  $[\text{Cu}_2(\eta^1: \eta^1\text{-B})_2(\eta^1\text{-CH}_3\text{CN})_4][\text{FAI}]_2$  (**5**) dimers. In addition, the  $\text{Cu}(\text{I})$  salt **2** reacts with **B** to afford selectively the heteroleptic dimer  $[\text{Cu}_2(\eta^1: \eta^1\text{-B})_2(\eta^1\text{-CH}_3\text{CN})_4][\text{TEF}]_2$  (**6**). The pristine dinuclear complexes **4-6** present promising building blocks for further supramolecular chemistry. Current investigations involve the replacement of the labile  $\text{CH}_3\text{CN}$  ligands by multitopic linkers to form new, extended organometallic-organic hybrid networks.

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## Conflicts of interest

There are no conflicts to declare.

## Notes and references

- 1 (a) S. T. Li, B. B. Cula, S. Hoof and C. Limberg, *Dalton Trans.*, 2018, **47**, 544; (c) S. Hanf, R. G. Rodríguez, S. Feldmann, A. D. Bond, E. H. Hawkins and D. S. Wright, *Dalton Trans.*, 2017, **46**, 814; (c) B. Hupp, C. Schiller, C. Lenczyk, M. Stanoppi, K. Edkins, A. Lorbach and A. Steffen, *Inorg. Chem.* 2017, **56**, 8996; (d) M. E. Moussa, S. Evariste, H.-L. Wong, L. Le Bras, C. Roiland, L. Le Polles, B. Le Guennic, K. Costuas, V. W.-W. Yam and C. Lescop, *Chem. Commun.*, 2016, **52**, 11370; (e) V. Gandin, F. Tisato, A. Dolmella, M. Pellei, C. Santini, M. Giorgetti, C. Marzano and M. Porchia, *J. Med. Chem.* 2014, **57**, 4745; (f) C. Marzano, V. Gandin, M. Pellei, D. Colavito, G. Papini, G. G. Lobbia, E. D. Giudice, M. Porchia, F. Tisato and C. Santini, *J. Med. Chem.* 2008, **51**, 798; g) A. A. Titov, O. A. Filippov, L. M. Epstein, N. V. Belkova and E. S. Shubina, *Inorg. Chim. Acta.* 2018, **470**, 22; h) A. A. Titov, A. F. Smol'yakov, O. A. Filippov, I. A. Godovikov, D. A. Muratov, F. M. Dolgushin, L. M. Epstein and E. S. Shubina, *Cryst. Growth Des.* 2017, **17**, 6770; i) O. A. Filippov, A. A. Titov, E. A. Guseva, D. A. Loginov, A. F. Smol'yakov, F. M. Dolgushin, N. V. Belkova, L. M. Epstein and E. S. Shubina, *Chem. Eur. J.* 2015, **21**, 13176.
- 2 (a) M. E. Moussa, S. Evariste, B. Krämer, R. Réau, M. Scheer and C. Lescop, *Angew. Chem. Int. Ed.*, 2018, **57**, 795; (b) G. A. Filonenko, R. R. Fayzullin and J. R. Khusnutdinova, *J. Mater. Chem. C*, 2017, **5**, 1638; (c) A. A. Melekhova, A. S. Novikov, T. L. Panikorovskii, N. A. Bokach and V. Y. Kukushkin, *New J. Chem.*, 2017, **41**, 14557; (d) S. C. Serin, F. S. Pick, G. R. Dake and D. P. Gates, *Inorg. Chem.* 2016, **55**, 6670; (e) B. P. Nell, C. D. Swor, E. A. Henle, L. N. Zakharov, N. I. Rinehart, A. Nathan and D. R. Tyler, *Dalton Trans.*, 2016, **45**, 8253; (f) H. Takeda, K. Ohashi, A. Sekine and O. Ishitani, *J. Am. Chem. Soc.* 2016, **138**, 4354; (g) W. Shen, M. E. Moussa, Y. Yao and C. Lescop, *Chem. Commun.*, 2015, **51**, 11560; h) M. E. Moussa, K. Guillois, W. Shen, R. Réau, J. Crassous and C. Lescop, *Chem. Eur. J.* 2014, **20**, 14853.
- 3 (a) A. Ilie, O. Crespo, M. C. Gimeno, M. C. Holthausen, A. Laguna, M. Diefenbach and C. Silvestru, *Eur. J. Inorg. Chem.* 2017, **20**, 2643; (b) J. Ortmeier, U. Flörke, G. Henkel, R. Wilhelm and A. Neuba, *Eur. J. Inorg. Chem.* 2017, **25**, 3191; (c) O. R. Wheelaghan, S. L. Aristizábal, J. L. Serrano, R. R. Fayzullin and R. Khusnutdinova, *Angew. Chem. Int. Ed.*, 2017, **56**, 16267; (d) K. Materne, S. Hoof, N. Frank, C. Herwig and C. Limberg, *Organometallics* 2017, **36**, 4891; (e) J. Qu, Y. Song, W. Ji, S. Jing, D. Zhu, W. Huang, M. Zheng, Y. Li and J. Ma, *Dalton Trans.*, 2016, **45**, 3417; (f) M. Fleishmann, L. Dütsch, M. E. Moussa, G. Balázs, W. Kremer, C. Lescop and M. Scheer, *Inorg. Chem.* 2016, **55**, 2840; (g) X. Wu, W. Zhang, X. Zhang, N. Ding and T. S. A. Hor, *Eur. J. Inorg. Chem.* 2015, **5**, 876; (h) C. Schwarzmaier, S. Heinel, G. Balázs and M. Scheer, *Angew. Chem. Int. Ed.* 2015, **54**, 13116; (i) G. Tan, B. Blom, D. Gallego and M. Driess, *Organometallics* 2014, **33**, 363.
- 4 S. F. Rach and F. E. Kühn, *Chem. Rev.* 2009, **109**, 2061.
- 5 (a) M. Fleishmann, S. Welsch, E. V. Peresyphkina, A. V. Virovets and M. Scheer, *Chem. Eur. J.* 2015, **21**, 14332; (b) G. S. Quiñones, A. Higelin, J. Schaefer, R. Brückner, C. Knapp and I. Krossing, *Chem. Eur. J.* 2009, **15**, 6663; (c) H.-C. Liang, E. Kim, C. D. Incarvito, A. L. Rheingold and K. D. Karlin, *Inorg. Chem.* 2002, **41**, 2209; (d) V. Zhuravlev and P. J. Malinowski, *Angew. Chem. Int. Ed.* 2018, **57**, 11697.
- 6 M. Scheer, *Dalton Trans.*, 2008, 4372-4386.
- 7 Selected publications: (a) M. E. Moussa, M. Fleishmann, E. V. Peresyphkina, L. Dütsch, M. Seidl, G. Balázs and M. Scheer, *Eur. J. Inorg. Chem.*, 2017, **25**, 3222; (b) C. Heindl, E. V. Peresyphkina, A. V. Virovets, W. Kremer and M. Scheer, *J. Am. Chem. Soc.* 2015, **137**, 10938; (c) F. Dielmann, C. Heindl, F. Hastreiter, E. V. Peresyphkina, A. V. Virovets, R. M. Gschwind and M. Scheer, *Angew. Chem. Int. Ed.* 2014, **53**, 13605; (d) E.-M. Rummel, M. Eckhardt, M. Bodensteiner, E. V. Peresyphkina, W. Kremer, C. Gröger and M. Scheer, *Eur. J. Inorg. Chem.*, 2014, **10**, 1625; (e) M. Scheer, A. Schindler, R. Merkle, B. P. Johnson, M. Linseis, R. Winter, C. E. Anson and A. V. Virovets, *J. Am. Chem. Soc.* 2007, **129**, 13386; (f) J. Bai, A. V. Virovets and M. Scheer, *Science* 2003, **300**, 781; (g) J. Bai, A. V. Virovets and M. Scheer, *Angew. Chem. Int. Ed.* 2002, **41**, 1737; (h) J. Bai, E. Leiner and M. Scheer, *Angew. Chem. Int. Ed.* 2002, **41**, 783.
- 8 (a) M. E. Moussa, S. Welsch, M. Lochner, E. V. Peresyphkina, A. V. Virovets and M. Scheer, *Eur. J. Inorg. Chem.*, 2018, **23**, 2689; (b) M. E. Moussa, S. Welsch, L. J. Gregoriades, G. Balázs, M. Seidl and M. Scheer, *Eur. J. Inorg. Chem.*, 2018, **15**, 1683; (c) M. E. Moussa, B. Attenberger, E. V. Peresyphkina and M. Scheer, *Dalton Trans.*, 2018, **47**, 1014; (d) M. E. Moussa, M. Seidl, G. Balázs, A. V. Virovets, B. Attenberger, A. Schreiner and M. Scheer, *Chem. Eur. J.* 2017, 16199; (e) M. E. Moussa, B. Attenberger, M. Fleischmann, A. Schreiner and M. Scheer, *Eur. J. Inorg. Chem.* 2016, **28**, 4538; (f) M. Elsayed Moussa, B. Attenberger, E. V. Peresyphkina, M. Fleischmann, G. Balázs and M. Scheer, *Chem. Commun.* 2016, **52**, 10004; (g) B. Attenberger, E. V. Peresyphkina and M. Scheer, *Inorg. Chem.*, 2015, **54**, 7021; (h) B. Attenberger, S. Welsch, M. Zabel, E. Peresyphkina and M. Scheer, *Angew. Chem. Int. Ed.*, 2011, **50**, 11516.
- 9 I. Csoregh, P. Kierkegaard, R. Norrestam, *Acta Crystallogr.* 1975, **B31**, 314.
- 10 M. Scheer, L. J. Gregoriades, M. Zabel, J. Bai, I. Krossing, G. Brunklaus and H. Eckert, *Chem. Eur. J.* 2008, **14**, 282.
- 11 S. Welsch, L. J. Gregoriades, M. Sierka, M. Zabel, A. V. Virovets and M. Scheer, *Angew. Chem. Int. Ed.* 2007, **46**, 9323.
- 12 (a) F. Dielmann, A. Schindler, S. Scheuermayer, J. Bai, R. Merkle, M. Zabel, A. V. Virovets, E. V. Peresyphkina, G. Brunklaus, H. Eckert, M. Scheer, *Chem. Eur. J.* 2012, **18**, 1168; (b) M. Scheer, A. Schindler, C. Gröger, A. V. Virovets, E. V. Peresyphkina, *Angew. Chem. Int. Ed.* 2009, **48**, 5046; (c) M. Scheer, J. Bai, B. P. Johnson, R. Merkle, A. V. Virovets, C. E. Anson, *Eur. J. Inorg. Chem.* 2005, **2005**, 4023.
- 13 O. J. Scherer, T. Brück, *Angew. Chem. Int. Ed.* 1987, **26**, 59.
- 14 Unpublished results.