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Unexpected Fragmentations of Triphosphaferrocene – Formation of Supramolecular Assemblies Containing the (1,2,4-$P_3C_2Mes_2$)$^-$ Ligand

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While reacting the sterically demanding triphosphaferrocene [Cp*Fe(η^5-$P_3C_2Mes_2$)] (**1**) with Cu(I) halides, the sandwich complex undergoes an unprecedented fragmentation into decamethylferrocene, FeX_2 (X = Cl, Br, I) and [$P_3C_2Mes_2$]$^-$ units. Subsequently, these phospholyl ligands act as versatile, negatively charged building blocks for the formation of supramolecular aggregates representing the monomeric, dimeric and polymeric (1D and 2D) coordination compounds [$(P_3C_2Mes_2)_2${$Cu_7(CH_3CN)_7(\mu_4$-X)(μ_3-X$)_2$(μ-X)}{$Cu_2(\mu_2$-X$)_2$X}{Cu(CH_3CN)(μ_2-X)}]$_2$ · 6 CH_3CN (**2** · 6 CH_3CN: X = Cl, **3** · 6 CH_3CN: X = Br), [$(P_3C_2Mes_2)_2${Cu(CH_3CN)}$_6$(μ-Br$)_2$(μ_3-Br$)_2${Cu($CH_3CN)_2$Br}$_2$] · CH_3CN (**4a** · CH_3CN), [$(P_3C_2Mes_2)_4${$Cu_5(CH_3CN)_5(\mu_2$-Br)}{Cu($CH_3CN)_2CuBr_2$}$_2${Cu($CH_3CN)_2$}]$_n^+$[$CuBr_2$]$_n^-$ · 2 CH_3CN (**5** · 2 CH_3CN), [($P_3C_2Mes_2$){Cu(CH_3CN)(μ-I)}$_4${Cu($CH_3CN)_3$}] · 0.5 C_7H_8 · 2.5 CH_3CN (**6** · 0.5 C_7H_8 · 2.5 CH_3CN), [($P_3C_2Mes_2$)$Cu_7(CH_3CN)_4(\mu_4$-I$)_2(\mu_3$-I$)_2(\mu$-I$)_2$]$_x$ · 2 C_7H_8 (**7** · 2 C_7H_8), [($P_3C_2Mes_2$){Cu($CH_3CN)_3$}$_2${Cu(μ-I)}$_6$] · 0.5 CH_2Cl_2 · 3 CH_3CN (**8** · 0.5 CH_2Cl_2 · 3 CH_3CN) and [Cp*Fe($CH_3CN)_3$]$_n^+$[$(P_3C_2Mes_2)_2${Cu($CH_3CN)_2$}{Cu(μ-I)}$_6$]$_n^-$ · 0.6 CH_2Cl_2 (**9** · 0.6 CH_2Cl_2) with rather non-typical structural motifs within the large varieties of the copper halide chemistry. Beside the X-ray structural analyses the obtained assemblies were also characterized in solution in which they undergo fragmentation and re-aggregation processes.

Introduction

Ferrocene [Fe(η^5-C_5H_5)$_2$] is one of the fundamental molecules in organometallic chemistry and until now the flood of publications devoted to its chemical properties does not stop. Apart from its use as a reference redox system (Fc/Fc$^+$),[1] chiral ferrocene-based ligands represent important classes of auxiliaries in asymmetric homogeneous catalysis.[2] Based on the isolobal principle the substitution of one up to six methine moieties by phosphorus atoms is possible, which gives rise to the class of phosphaferrocenes.[3] These 18 VE sandwich complexes turned out to be very stable and, in contrast to ferrocene, the lone pairs of the P atoms enable them to be excellent building blocks in coordination and supramolecular chemistry.[4] Therefore new perspectives for the synthesis of phosphorus-based oligomers and polymers open up.

For the aggregation of these organometallic moieties we have

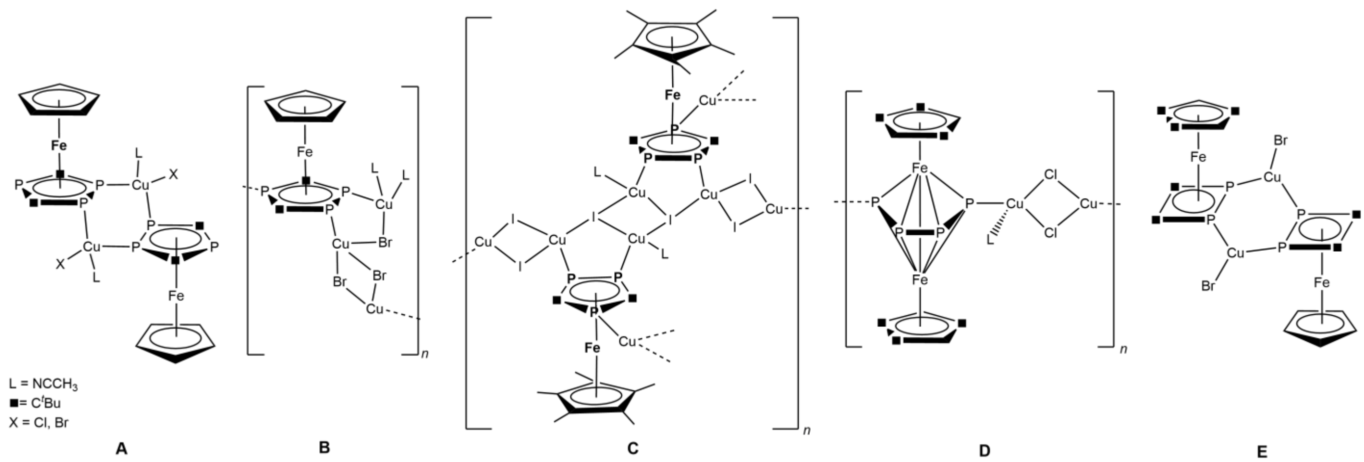

Fig. 1 Coordination compounds of triphosphaferrocenes [Cp^{R}Fe(η^5-$P_3C_2{}^tBu_2$)] (Cp^R = Cp, Cp*, Cp''') and Cu(I) halides.

broadly used Cu(I) halides.[5] To combine the central role of copper in catalysis[6] with the potential of phosphaferrocenes in this area,[3b] it is of special interest to accumulate copper halides by phosphaferrocenes. For such a purpose the 1,2,4-triphosphaferrocene $[Cp^{R}Fe(\eta^5\text{-}P_3C_2{}^{t}Bu_2)]$ (Cp^R = Cp, Cp*, Cp'''; Cp* = C_5Me_5; Cp''' = $C_5H_2{}^{t}Bu_3$) with three possible coordination sites is suited very well. Recently, we have shown that its coordination behaviour strongly depends on the steric demand of the adjacent Cp^R ring and the nature of the halide.[7]

A selection of the obtained structural motifs is shown in Figure 1. Using less bulky Cp^R ligands (Cp^R = Cp, Cp*) the coordination of two or even three phosphorus atoms leads to the formation of dimeric (**A**) and polymeric compounds (**B** and **C**).[7a,b] However, the use of Cp''' leads to a much higher steric demand of the triphosphaferrocene, hence different products could be obtained. Beside a complex similar to **A** was formed, two unexpected fragmentation reactions of the $P_3C_2{}^{t}Bu_2$ ring took place. Treating $[Cp'''Fe(\eta^5\text{-}P_3C_2{}^{t}Bu_2)]$ with an excess of CuCl a polymeric chain containing triple decker moieties $[(FeCp''')_2(\mu,\eta^4{:}\eta^4\text{-}P_4)]$ is formed (**D**).[7c] In **D** formally a C_2P moiety was replaced by one phosphorus atom, hence in the resulting diphosphacyclobutadiene ring in **E** a formal elimination of a P atom occurred.[7a]

Since the substitution pattern of the Cp^R ligand seems to play a determining role, the question arises, whether a change of the steric demand of the triphospholyl ligand itself would cause consequences. Hence, instead of the *tert*-butyl groups, we decided to use $[Cp^{*}Fe\{\eta^5\text{-}(1,2,4\text{-}P_3C_2Mes_2)\}]$ (Mes = 2,4,6-trimethylphenyl) (**1**)[8] with two sterically even more demanding mesityl groups next to the phosphorus atoms and explore its coordination behaviour towards Cu(I) halides.

Herein we report on the unexpected fragmentation of **1** by the reaction with CuX (X = Cl, Br, I) yielding a large diversity of unprecedented coordination compounds and show the usefulness of the formed $P_3C_2Mes_2^-$ five-membered ring as a building block for extended structures in:

$[(\mu,\eta^1{:}\eta^2{:}\eta^2\text{-}P_3C_2Mes_2)(\mu,\eta^1{:}\eta^3{:}\eta^3\text{-}P_3C_2Mes_2)\{Cu_7(CH_3CN)_7(\mu_4\text{-}X)(\mu_3\text{-}X)_2(\mu\text{-}X)\}\{Cu_2(\mu_2\text{-}X)_2X\}\{Cu(CH_3CN)(\mu_2\text{-}X)\}]_2 \cdot 6\,CH_3CN$ (**2** $\cdot$ 6 CH_3CN**:** X = Cl, **3** $\cdot$ 6 CH_3CN**:** X = Br),

$[(\mu,\eta^1{:}\eta^2{:}\eta^3\text{-}P_3C_2Mes_2)_2\{Cu(CH_3CN)\}_6(\mu\text{-}Br)_2(\mu_3\text{-}Br)_2\{Cu(CH_3CN)_2Br\}_2] \cdot CH_3CN$ (**4a** $\cdot$ CH_3CN),

$[(\mu,\eta^1{:}\eta^1{:}\eta^2\text{-}P_3C_2Mes_2)_3(\mu,\eta^1{:}\eta^2{:}\eta^3\text{-}P_3C_2Mes_2)\{Cu_5(CH_3CN)_5(\mu_2\text{-}Br)\}\{Cu(CH_3CN)_2CuBr_2\}_2\{Cu(CH_3CN)_2\}]_n{}^{+}[CuBr_2]_n{}^{-} \cdot 2\,CH_3CN$ (**5** $\cdot$ 2 CH_3CN),

$[(\mu,\eta^1{:}\eta^2{:}\eta^2\text{-}P_3C_2Mes_2)\{Cu(CH_3CN)(\mu\text{-}I)\}_4\{Cu(CH_3CN)_3\}] \cdot 0.5\,C_7H_8 \cdot 2.5\,CH_3CN$ (**6** $\cdot$ 0.5 C_7H_8 $\cdot$ 2.5 CH_3CN),

$[(\mu,\eta^1{:}\eta^2{:}\eta^2\text{-}P_3C_2Mes_2)Cu_7(CH_3CN)_4(\mu_4\text{-}I)_2(\mu_3\text{-}I)_2(\mu\text{-}I)_2]_x \cdot 2\,C_7H_8$ (**7** $\cdot$ 2 C_7H_8),

$[(\mu,\eta^1{:}\eta^3{:}\eta^3\text{-}P_3C_2Mes_2)\{Cu(CH_3CN)_3\}_2\{Cu(\mu\text{-}I)\}_6] \cdot 0.5\,CH_2Cl_2 \cdot 3\,CH_3CN$ (**8** $\cdot$ 0.5 CH_2Cl_2 $\cdot$ 3 CH_3CN) and

$[Cp^{*}Fe(CH_3CN)_3]_n{}^{+}[(\mu,\eta^1{:}\eta^3{:}\eta^3\text{-}P_3C_2Mes_2)_2\{Cu(CH_3CN)_2\}\{Cu(\mu\text{-}I)\}_6]_n{}^{-} \cdot 0.6\,CH_2Cl_2$ (**9** $\cdot$ 0.6 CH_2Cl_2).

Results and Discussion

Coordination behaviour of 1 towards Cu(I) halides – Unexpected Fragmentation

The self-assembly process of **1** and CuX (X = Cl, Br, I) leads to different coordination compounds depending on the conditions applied. Surprisingly, building block **1** always underwent fragmentation. Out of the fragmentation products, only the 1,2,4-triphospholyl ligand remains in the isolated products, hence the $[Cp^{*}Fe]^{+}$ unit must have been split off. These fragments together with remaining halide anions might initially form the dimeric complex $[Cp^{*}Fe(\mu\text{-}X)]_2$ (X = Cl, Br, I), which displays a known intermediate and can even be isolated, when Cp^R ligands with a higher steric demand are used.[9] Since this compound is coordinatively unsaturated, it, in all probability, dissociates into $[Cp^{*}{}_2Fe]$ and $FeBr_2$. To support this assumption, the reaction mixtures were analysed by ^1H NMR spectroscopy and mass spectrometry. In fact, a singlet at 1.64 ppm in the ^1H NMR spectra can be assigned for $[Cp^{*}{}_2Fe]$ and the EI mass spectra display peaks corresponding to decamethylferrocene as well. In addition, the negative ion ESI mass spectra of the mother liquors exhibit peaks for $[FeCl_3]^-$ and $[FeBr_3]^-$, respectively.

Among the stable phosphaferrocenes the rather uncommon fragmentations are mostly related to the cleavage of C-P bonds in the phospholyl ligands (**D** and **E**). Hence, the unexpected instability of **1** is unique and can most likely be attributed to the influence of the bulky mesityl ligand. This is confirmed by the existence of a stable $[P_3C_2Mes^{*}{}_2]$ (Mes* = 2,4,6-tri-*tert*-butylphenyl) radical, reported by Ionkin et al, by using the similar, sterically even more demanding Mes* moiety.[10]

Solid-State Characterization of the Coordination Compounds

All isolated coordination compounds contain the remaining negatively charged $[P_3C_2Mes_2]^-$ unit as a building block. So far, the cyclic 1,2,4-triphospholyl ligand was mainly used for the synthesis of (half-)sandwich complexes.[11] Its coordination behaviour towards Lewis acids, especially coinage metal salts, has rather been neglected, although interesting coordination modes to gold centres have been observed by reaction with $[(PPh_3)AuCl]$ and $[(PEt_3)AuCl]$, respectively.[12] However concerning Cu, to the best of our knowledge, only two reactions are known: Nixon *et al.* treated $K[P_3C_2{}^{t}Bu_2]$ with Cu_2I_2 in presence of PMe_3, yielding the binuclear complexes $[\{P_3C_2{}^{t}Bu_2\}\{Cu(PMe_3)_2\}_2I]$ and $[\{P_3C_2{}^{t}Bu_2\}_2\{Cu(PMe_3)_2\}_2]$.[12b] Zenneck et al. succeeded in the synthesis of the versatile $[\{\eta^5\text{-}(P_3C_2{}^{t}Bu_2)\}Cu(PPh_3)]$ complex.[13]

In general, Cu(I) halides display versatile building blocks in coordination chemistry, and therefore a large variety of different coordination compounds can be obtained. Since the structural motifs differ when different halides are used, they will be described separately.

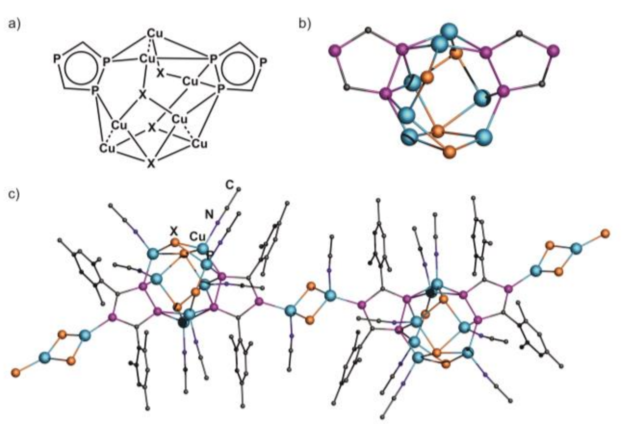

Fig. 2 a) 'Cage' motif in **2** $\cdot$ 6 CH_3CN (X = Cl) and **3** $\cdot$ 6 CH_3CN (X = Br), b) Section of the molecular structure of **2** $\cdot$ 6 CH_3CN illustrating the 'cage' motif, c) Molecular structure of the dimer of **2** $\cdot$ 6 CH_3CN. H atoms and solvent molecules are omitted for clarity.

CuCl-containing Compound (2)

The reaction of **1** with CuCl selectively leads to the formation of the dimeric complex $[(\mu,\eta^1:\eta^2:\eta^2\text{-}P_3C_2Mes_2)(\mu,\eta^1:\eta^3:\eta^3\text{-}P_3C_2Mes_2)\{Cu_7(CH_3CN)_7(\mu_4\text{-}Cl)(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)\}\{Cu_2(\mu_2\text{-}Cl)_2Cl\}\{Cu(CH_3CN)(\mu_2\text{-}Cl)\}]_2$ (**2**), which can be isolated as solvate **2** · 6 CH_3CN in quantitative yields (Fig. 2c).

Compound **2** · 6 CH_3CN displays a dimer of two central $[P_3C_2Mes_2]_2Cu_7Cl_4$ cages (Fig. 2a,b), which are bridged by a $\{Cu(CH_3CN)\}_2Cl_2$ four-membered ring formed by tetrahedrally coordinated copper ions. The unique P atom of the peripheral $[P_3C_2Mes_2]$ fragment is additionally coordinated at each side of the dimer by a terminal Cu_2Cl_3 fragment, in which the threefold-coordinated copper ions are in a triangular planar environment. In total, four $[P_3C_2Mes_2]^-$ rings and 16 Cl^- balance the positive charge of 20 Cu^+. The central structural motif can be described as an unprecedented cage of 15 inorganic atoms (4 P, 7 Cu, 4 Cl), consisting of one Cu ion and three Cu_2 dimers (2.546(1) - 2.617(1) Å), connected by a μ_2-Cl, two μ_3-Cl and one μ_4-Cl (2.303(1) – 2.840(1) Å). The unique phosphorus atom of the $[P_3C_2Mes_2]^-$ ligand is η^1-coordinated to copper (2.173(1) – 2.153(1) Å), while the adjacent P atoms each show a η^2- and η^3-coordination with longer Cu–P distances to two Cu_2 dimers and two Cu_2 dimers and one unique Cu ion, respectively. The Cu-P distances involving Cu_2 dimers (2.221(1) – 2.406(1) Å) are systematically shorter than those to the unique Cu ion (2.419(1) – 2.501(1) Å) (see also SI and Table 1). The P_3C_2 rings of the phospholyl ligands are planar (deviation 0.01°) with the mesityl ligands rotated by 82.6° and 72.6° at the peripheral phospholyl rings and of 89.1° and 79.9° in the central ones, respectively. Thus, the rotation is much more distinctive than in **1** (46.07(1)° and 40.85(1)°, respectively),[8] most likely due to the absence of a Cp* ligand.

CuBr-containing Compounds (3-5)

Diffusion of a CH_3CN solution of CuBr into a CH_2Cl_2 solution of **1** leads to the crystallization of three different coordination compounds depending on the applied conditions: $[(\mu,\eta^1:\eta^2:\eta^2\text{-}P_3C_2Mes_2)(\mu,\eta^1:\eta^3:\eta^3\text{-}P_3C_2Mes_2)\{Cu_7(CH_3CN)_7(\mu_4\text{-}Br)(\mu_3\text{-}Br)_2(\mu\text{-}Br)\}\{Cu_2(\mu_2\text{-}Br)_2Br\}\{Cu(CH_3CN)(\mu_2\text{-}Br)\}]_2$ · 6 CH_3CN (**3** · 6 CH_3CN), $[(\mu,\eta^1:\eta^2:\eta^3\text{-}P_3C_2Mes_2)_2\{Cu(CH_3CN)\}_6(\mu_2\text{-}Br)_2(\mu_3\text{-}Br)_2\{Cu(CH_3CN)_2Br\}_2]$ · CH_3CN (**4a** · CH_3CN), $[(\mu,\eta^1:\eta^1:\eta^2\text{-}P_3C_2Mes_2)_3(\mu,\eta^1:\eta^2:\eta^3\text{-}P_3C_2Mes_2)\{Cu_5(CH_3CN)_5(\mu_2\text{-}Br)\}\{Cu(CH_3CN)_2CuBr_2\}_2\{Cu(CH_3CN)_2\}]_n^+[CuBr_2]_n^-$ · 2 CH_3CN (**5** · 2 CH_3CN**)**. If a molar ratio of **1**:CuBr = 1:2 is used, compound **5** · 2 CH_3CN is formed selectively, which is in agreement with the stoichiometric ratio of $(P_3C_2Mes_2)$:Cu = 1:2 in **5** · 2 CH_3CN. Excess of CuBr (1:5 or 1:10) therefore enables the assembly to **3** and **4**. However, since the ratio $(P_3C_2Mes_2)$:Cu is the same in **3** and **4** (1:5), a selective synthesis is rather difficult. Nonetheless a preferred crystallization of **4** · CH_3CN is achieved by applying more diluted and pure CH_3CN solutions, while the use of more concentrated and CH_2Cl_2/CH_3CN solvent mixtures favours crystallization of **3** · 6 CH_3CN. Compound **3** · 6 CH_3CN is isostructural to the Cl derivative **2** · 6 CH_3CN (Fig. 2). The bond distances in **3** · 6 CH_3CN remain in a similar range despite the presence of the larger halogen anion (see Table 1).

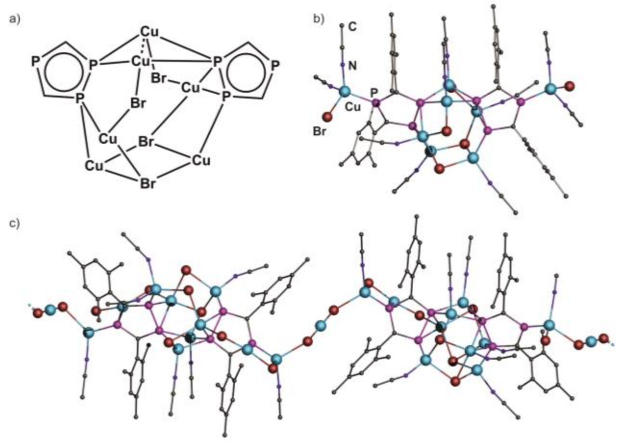

Fig. 3 a) 'Cage' motif in **4a** · CH_3CN, b) Molecular structure of **4a** · CH_3CN, c) Section of the polymeric structure of **4a** · CH_3CN. H atoms and solvent molecules are omitted for clarity.

Surprisingly, the X-ray structural analysis of **4** · CH_3CN reveals a solid solution of different compounds attended with partial occupancies and complex disorder of the Cu, Br and CH_3CN positions. The monomeric compound $[\{\mu,\eta^1:\eta^2:\eta^3\text{-}(P_3C_2Mes_2)\}_2\{Cu(CH_3CN)\}_6(\mu_2\text{-}Br)_2(\mu_3\text{-}Br)_2\{Cu(CH_3CN)_2Br\}_2]$ (**4a** · CH_3CN) displays the structural fragment with major occupation (70%) (Fig. 3b). The central cage motif in **4a** · CH_3CN is structurally related to those of the dimer **3** · 6 CH_3CN with one missing $Cu(CH_3CN)$ unit to give a formally neutral $\{(P_3C_2Mes_2)_2Cu_6Br_4\}$ cage (Fig. 3a). This difference influences the connectivity and bond lengths, hence the Br ions connect the Cu ions in a μ_2-(2 Br) or a μ_3-fashion (2 Br) (2.431(1) – 2.592(1) Å), respectively. The coordination mode of the adjacent P atoms to Cu is also different, one is η^2-, the other η^3-coordinated within a more extensive range of the distances (2.202(2) – 2.521(2) Å). In **4a** · CH_3CN only one Cu_2 dimer is present with a distance of 2.533(1) Å compared to three dimers in **3**. The unique phosphorus atoms each coordinate a $\{Cu(CH_3CN)_2Br\}$ unit instead of the Cu_2Br_3 unit in **3** · 6 CH_3CN. Other similar structural fragments of the solid solution **4** · CH_3CN with minor occupation factors are possible (for more information see SI), among them even the polymeric compound $[(P_3C_2Mes_2)_2Cu_{11}Br_9(MeCN)_7]_x$ (**4b** · CH_3CN) (occupation factor 10%) containing a linear coordinated Cu (Cu-Br: 2.226(4) Å) (Fig. 3c) co-exists.

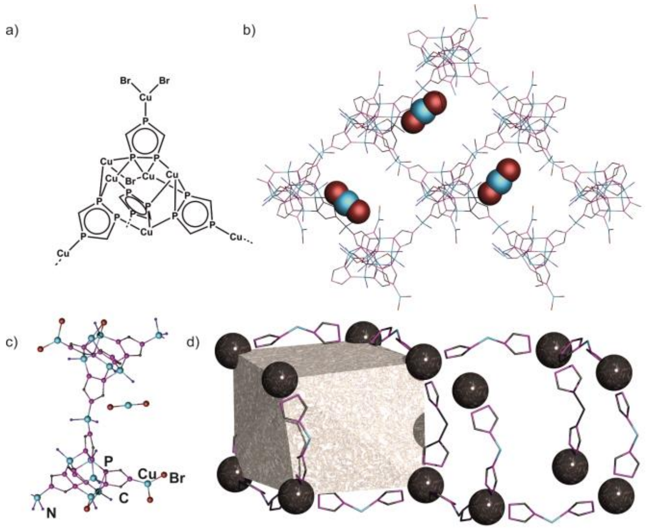

Fig. 4: a) ‘Cage’ motif in **5** · 2 CH_3CN, b) Section of the polymeric structure of **5** · 2 CH_3CN illustrating the mesh-like structure (view along the crystallographic a-axis). The anions are displayed in the space-filling model, the network in ‘wires and sticks’. H atoms, mesityl ligands and solvent molecules are omitted for clarity. c) Repeating unit in **5** · 2 CH_3CN. H atoms, mesityl ligands and solvent molecules are omitted for clarity. d) Schematic representation of the cube-like arrangement of a single layer in **5** · 2 CH_3CN.

While with CuCl the used molar ratio does not influence the product formation, with CuBr **5** · 2 CH_3CN can be obtained selectively and reproducible, when less than five equivalents of CuBr are used. Its structural analysis reveals a 2D network, which is rather astonishing in consideration of the bulky mesityl substituents. A totally different cage motif again demonstrates the versability of the phospholyl ligand and CuBr in coordination chemistry. The central core contains four $[P_3C_2Mes_2]$ units (Fig. 4a), whose adjacent P atoms coordinate two Cu_2 dimers (2.527(2) – 2.663(2) Å) and one single Cu in either an η^1 (3 P; 2.239(2) – 2.282(2) Å), η^2 (4 P; 2.282(2) – 2.538(2) Å) or an η^3 (1 P; 2.331(2) – 2.469(2) Å) coordination mode. In addition, one Br bridges two Cu atoms with a distance of 2.295(2) – 2.350(2) Å, resulting in a distorted tetrahedral environment for these Cu. One of the four unique P atoms is linked to a terminal $\{CuBr_2\}$ unit with a trigonal planar Cu, which blocks further growth into this direction, while the other three coordinate a $\{Cu(CH_3CN)_2\}$ unit, whereby polymerization is enabled. The repeating unit (two ‘cages’ plus the linking and terminal moieties) therefore consists of eight $[P_3C_2Mes_2]^-$, six Br^- and 15 Cu^+. Its remaining charge is balanced by a linear dibromocuprate counter ion $[CuBr_2]^-$ (Fig. 4c). The 2D network of **5** · 2 CH_3CN can be described as a sheet-like structure with porous layers. A single layer consists of ‘cubes’ out of four repeating units stringing together (Fig. 4d). Since in one direction polymerization is hindered due to the terminal $\{CuBr_2\}$ unit, four edges per cube are absent. The view along the crystallographic a-axis illustrates the resulting mesh-like structure (Fig. 4b). However, these meshes display no empty voids, but are occupied by the mesityl ligands and the counter anion.

CuI-containing Compounds (6-9)

By combining **1** and CuI, products with two different very rare structural motifs of CuI units can be realized, the ‘crown’ (Fig. 5a) and the ‘hexagram’ motif (Fig. 7a). Both are found either in a monomeric coordination compound or in a 1D polymer: $[(\mu,\eta^1:\eta^2:\eta^2\text{-}P_3C_2Mes_2)\{Cu(CH_3CN)(\mu_2\text{-}I)\}_4\{Cu(CH_3CN)_3\}]$ · 0.5 C_7H_8 · 2.5 CH_3CN (**6** · 0.5 C_7H_8 · 2.5 CH_3CN), $[(\mu,\eta^1:\eta^2:\eta^2\text{-}P_3C_2Mes_2)Cu_7(CH_3CN)_4(\mu_4\text{-}I)_2(\mu_3\text{-}I)_2(\mu_2\text{-}I)_2]_x$ · 2 C_7H_8 (**7** · 2 C_7H_8), $[(\mu,\eta^1:\eta^3:\eta^3\text{-}P_3C_2Mes_2)\{Cu(CH_3CN)_3\}_2\{Cu(\mu_2\text{-}I)\}_6]$ · 0.5 CH_2Cl_2 · 3 CH_3CN (**8** · 0.5 CH_2Cl_2 · 3 CH_3CN) and $[Cp^*Fe(CH_3CN)_3]_n{}^+[(\mu,\eta^1:\eta^3:\eta^3\text{-}P_3C_2Mes_2)_2\{Cu(CH_3CN)_2\}\{Cu(\mu_2\text{-}I)\}_6]_n{}^-$ · 0.6 CH_2Cl_2 (**9** · 0.6 CH_2Cl_2). A controlled and selective synthesis of one specific compound is a big challenge due to similar molar ratios (($P_3C_2Mes_2$):Cu = 1:5, 1:7, 1:8 and 1:7 in **6**, **7**, **8** and **9**, respectively) in the products. However, it has never occurred that products with different structural motifs crystallize out of one sample. Hence, either the crystallization of one single compound or of mixtures of **6** · 0.5 C_7H_8 · 2.5 CH_3CN and **7** · 2 C_7H_8 or **8** · 0.5 CH_2Cl_2 · 3 CH_3CN and **9** · 0.6 CH_2Cl_2 can be obtained, respectively. The crystallization of solely **7** (polymer) is obtained when a pure CH_3CN solution is used. In conclusion, pure **6** · 0.5 C_7H_8 · 2.5 CH_3CN (monomer) is obtained as the only crystalline product applying CH_2Cl_2/CH_3CN solvent mixtures or more diluted conditions, which has been proved reproducible. Additionally an excess of **1** is conducive, since in **6** · 0.5 C_7H_8 · 2.5 CH_3CN the lowest Cu content is present. Unfortunately, the formation of **9** has only been observed on very rare occasions together with **8** · 0.5 CH_2Cl_2 · 3 CH_3CN. Several attempts to reproduce this compound only resulted in the selective isolation of **8** · 0.5 CH_2Cl_2 · 3 CH_3CN, independent of the solvents and crystallization procedures.

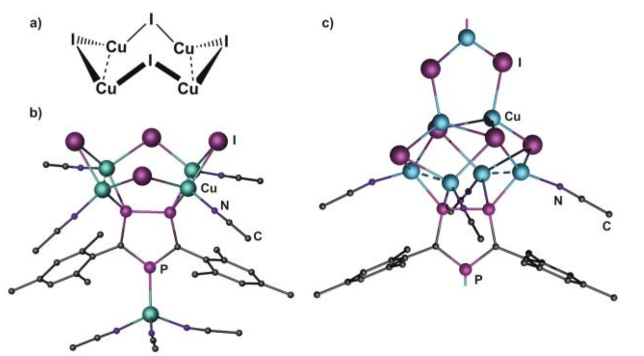

Fig. 5 a) ‘Crown’ structural motif in **6** · 0.5 C_7H_8 · 2.5 CH_3CN and **7** · 2 C_7H_8, b) Molecular structure of **6** · 0.5 C_7H_8 · 2.5 CH_3CN, c) Repeating unit of the polymeric structure of **7**. H atoms and the minor position of the disordered mesityl ligand are omitted for clarity.

The ‘crown’ motif in **6** · 0.5 C_7H_8 · 2.5 CH_3CN consists of an eight-membered Cu_4I_4 ring which is significantly distorted by the presence of two opposed Cu_2 dimers (2.556(1) – 2.561(1) Å) which are separated by 4.030(1)-4.032(1) Å one from another (Fig. 5b). The copper atoms of each dimer are coordinated by the adjacent P atoms of the phospholyl ligands (2.292(1) -2.313(1) Å). In contrast, the third P atom again shows a η^1-coordination to a single Cu ion revealing a shorter bond length of 2.217(1) Å, as it was observed in the previous discussed compounds (for a comparison of selected bond lengths see Table 1). The tetrahedral coordination of Cu is accomplished by CH_3CN ligands. The presence of five Cu^+, four I^- and one $[P_3C_2Mes_2]^-$ ligand affords charge balance.

By formally replacing three CH_3CN ligands at the terminal Cu ion by two CuI fragments, **6** serves as repeating unit for the 1D polymer **7** · 2 C_7H_8 (Fig. 5c, Fig. 6). The geometry of the ‘crown’ fragment retains similar Cu-P distances (2.235(2) – 2.428(3) Å) and Cu-I (2.657(2) – 2.864(2) Å), but the Cu···Cu separations became significantly more uniform, 2.688(2) and 3.664(2) Å (Fig. 7S, Table

1), respectively. To bridge these units, an additional five-membered Cu_3I_2 ring is formed, and another Cu_2 dimer (Cu···Cu 2.876(1) Å) coordinates an iodide of the 'crown'. In **7**, the iodine atoms do not bridge only two Cu ions as in **6** · 0.5 C_7H_8 · 2.5 CH_3CN, but show a μ_3 and μ_4-coordination mode, respectively. A neutral coordination polymer results, since the repeating unit contains seven Cu^+, six I^- and one $[P_3C_2Mes_2]^-$ ligand. The rotation of the mesityl ligands with respect to the phospholyl plane is comparable to **2** · 6 CH_3CN with angles of 89.5° in **7** · 2 C_7H_8 and 84.1° and 83.8° in **6** · 0.5 C_7H_8 · 2.5 CH_3CN, respectively.

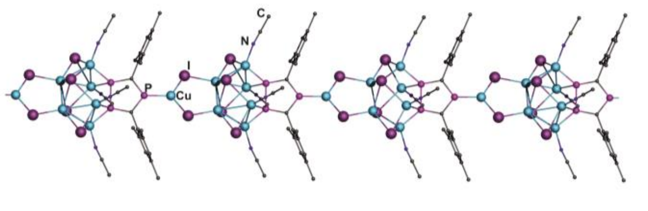

Fig. 6 Section of the polymeric structure of **7** · 2 C_7H_8. H atoms, disorder and solvent molecules are omitted for clarity.

The Cu_4I_4 'crown' motif in **6** and **7** is uncommon, since this number of CuI units usually prefers a cubane- or step-like arrangement.[14] Its formation was only observed once by Sugimoto et al., and in this case the copper ions are coordinated by sulfur atoms.[15]

Among the large variety of CuX (X = Cl, Br, I) coordination compounds in the literature, only one example is known for the 'hexagram' structural motif: $[\{(triphos)\text{-}CoP_3\}_2\{CuBr\}_6]$ (triphos = $MeC(CH_2PPh_2)_3$).[16] Hence, **8** and **9** represent the first examples with an iodine-containing hexagonal core.

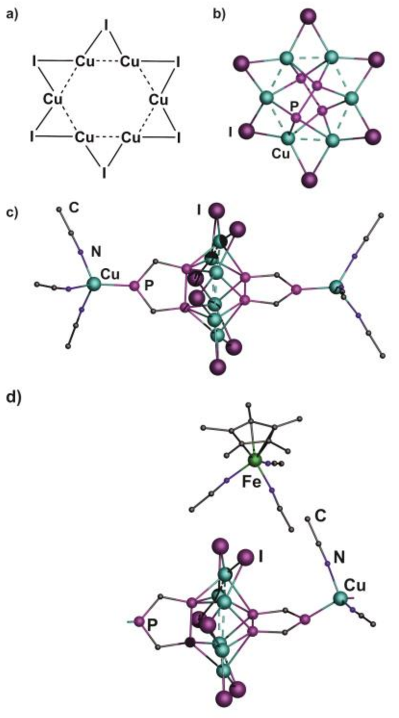

Fig. 7 a) 'Hexagram' structural motif in **8** · 0.5 CH_2Cl_2 · 3 CH_3CN and **9** · 0.6 CH_2Cl_2, b) section of the molecular structure of **8** · 0.5 CH_2Cl_2 · 3 CH_3CN (top view) illustrating the 'hexagram' motif, c) molecular structure of **8** · 0.5 CH_2Cl_2 · 3 CH_3CN, d) repeating unit of the polymeric structure of **9** · 0.6 CH_2Cl_2. H atoms, mesityl ligands and solvent molecules are omitted for clarity.

The central almost planar Cu_6 ring (deviation 0.12 Å) is coordinated by two phospholyl ligands, which are rotated to each other by 66.6° (Fig. 7b). Each of the adjacent P atom shows a η^3-coordination mode towards Cu with bond lengths of 2.304(4) – 2.820(4) Å. As in the case of Cu_2 dimers in **2**-**7**, Cu···Cu interactions may be considered in **8** · 0.5 CH_2Cl_2 · 3 CH_3CN as well, since the Cu···Cu distances are in the range of 2.471(3) – 2.553(3) Å.[17] Six I ions bridge these edges in a μ_2-fashion (2.550(2) – 2.627(2) Å) so that a distorted 'hexagram' structural motif is formed. This core structure is completed by two terminal $\{Cu(CH_3CN)_3\}$ units, which coordinate the remaining P atoms (Fig. 7c). With eight Cu^+, six I^- and two $[P_3C_2Mes_2]^-$ ligands **8** · 0.5 CH_2Cl_2 · 3 CH_3CN also displays a neutral molecular complex.

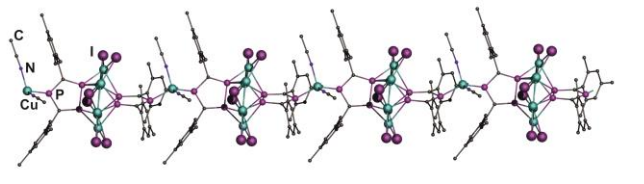

Fig. 8 Section of the anionic polymeric structure of **9**. H atoms and minor disordered components are omitted for clarity.

Removing formally one $\{Cu(CH_3CN)_3\}$ unit and CH_3CN ligand from different sides of the molecular complex **8**, the resulting complex forms the negatively charged repeating unit of the 1D polymer **9** · 0.6 CH_2Cl_2 without significant changes concerning the 'hexagram' motif (Fig. 7d, Fig. 8). The Cu-Cu and Cu-I bond lengths vary in ranges of 2.454(2)–2.535(2) and 2.537(1)–2.617(1) Å, respectively (see also SI). The Cu-P bonds are slightly shorter within the range of 2.251(2)–2.778(2) Å (For a comparison of selected bond lengths see Table 1). Surprisingly, $[Cp^*Fe(CH_3CN)_3]^+$ turned out to act as counter ion, which is known as an extremely water-sensitive complex with very labile acetonitrile ligands.[18] Hence, another reaction pathway of the $[Cp^*Fe]^+$ cation aforesaid becomes apparent in this case, namely the accomplishment of the free coordination sites by acetonitrile ligands.

Table 1 Selected bond lengths [Å] of **2**-**9**. Ranges of bond lengths are given whenever more than one bond is present in the asymmetric unit.

	X	Cu···Cu	Cu-P_{unique}	Cu_{dimer}-P	Cu_{unique}-P	Cu-X
2	Cl	2.564(1) – 2.617(1)	2.153(1) – 2.173(1)	2.221(1) – 2.406(1)	2.419(1) – 2.501(1)	2.303(1) – 2.840(1)
3	Br	2.531(1) – 2.599(1)	2.169(2) – 2.189(2)	2.230(2) – 2.386(2)	2.420(2) – 2.514(2)	2.291(1) – 2.660(1)
4a	Br	2.533(1)	2.219(2)	2.202(2) – 2.521(2)	2.202(2) – 2.521(2)	2.431(1) – 2.592(1)
5	Br	2.527(2) – 2.663(2)	2.239(2) – 2.282(2)	2.239(2) – 2.538(2)	2.266(3) – 2.373(3)	2.295(2) – 2.350(2)
6	I	2.556(1) – 2.561(1)	2.217(1)	2.292(1) – 2.313(1)	-	2.633(1) – 2.694(1)
7	I	2.688(2) – 2.876(1)	2.191(3)	2.235(2) – 2.428(3)	-	2.657(2) – 2.864(2)
8	I	2.471(3) – 2.553(3)	2.202(4) – 2.218(4)	2.304(4) – 2.820(4)	-	2.550(2) – 2.627(2)
9	I	2.454(2) – 2.535(2)	2.256(2)	2.251(2) – 2.778(2)	-	2.537(1) – 2.617(1)

Spectroscopic characterization of the products

All obtained compounds **2**-**9** are completely insoluble in non-polar solvents like *n*-hexane or toluene as well as in more polar solvents like CH_2Cl_2 and Et_2O. But they all show solubility in CH_3CN up to a certain degree, which enables their characterization in solution by NMR spectroscopy as well as by mass spectrometry. The solubility decreases when going to the heavier halides, but the lowest solubility is found for **5** due to its 2D polymeric structure (characterization in solution by ^1H and mass spectrometry only). The $^{31}P\{^1H\}$ NMR spectrum of **3** in CD_3CN shows four very broad signals at δ = 136, 160, 204 and 217 ppm with integral ratios of 4:6:3:2. The broadening of the signals implies that the coordination of the P atoms to Cu (nuclear spin I = 3/2) is still present in solution. In contrast to **1** (δ = 73.2 ppm)[8] the signals show a strong downfield shift, though this comparison is hampered, since no coordination to Fe is present in the product. In contrast, the signals of **3** are shifted to higher field when compared to the free phospholyl ligand in $K[P_3C_2Mes_2]$ (δ = 261.7 and 266.4 ppm).[8] This is in agreement with the observations made for other coordination compounds starting from different P_n ligand complexes and Cu(I) halides.[19] However, to explain the integral ratios of the observed signals, one must assume the presence of two different compounds in solution. In addition, the $^{31}P\{^1H\}$ NMR spectrum of freshly dissolved crystals of pure **4** · CH_3CN surprisingly looks exactly the same with minimal differences in the integral ratio (δ = 135, 160, 205 and 217 ppm with integral ratios of 4:5:2.5:2). Since elemental analyses confirm the purity of the respective products, these results imply dynamic dis- and re-assembly behaviour in solution. In addition, for a plausible assignment variable temperature $^{31}P\{^1H\}$ NMR spectra of crystals of **3** · 6 CH_3CN were recorded (spectra see SI). Upon cooling to 273 K the outer signals at δ = 135 and 217 ppm get sharpened and increase by intensity. In contrast, the intensity of the inner signals at δ = 160 and 204 ppm decrease and vanish completely upon further cooling to 253 K. The opposite effect, namely the disappearance of the outer signals, is monitored when the sample is heated to 343 K. Therefore the inner signals can be attributed to a rather small, monomeric unit, since its formation requires bond dissociations, which are forced by higher temperatures. In contrast, cooling favours the existence of larger aggregates, hence the outer signals are assigned to dimeric or oligomeric coordination compounds. The values for the integral ratios are in accordance with this, each group being 2:1 for the adjacent and the unique P atoms, respectively. These dynamic processes are further confirmed by mass spectrometry. In the received positive ion ESI spectra many different fragments from $[\{P_3C_2Mes_2\}Cu_5Br_3\{CH_3CN\}]^+$ up to $[\{P_3C_2Mes_2\}_4Cu_{17}Br_{12}]^+$ can be identified.

The behaviour in solution does not depend on the used halide, since the same observations were made for compounds **2** and **6**-**9**. Interestingly, the $^{31}P\{^1H\}$ NMR spectrum of dissolved crystals of **2** also looks similar like compound **3**, but after many attempts no second compound could be isolated, most probably due to the preferred crystallization of **2**.

Furthermore, it should be noted that in the $^{31}P\{^1H\}$ NMR spectra of the CuI-containing assemblies **6**-**9** the signals exhibit the same chemical shift like **2**-**4** despite their different structural motifs in the solid state: ‘crown’ (**6**,**7**) and ‘hexagram’ (**8**,**9**) motif compared to the ‘cage’ motif (**2**-**4**). However, the quality of the received spectra is initially quite poor caused by the low solubility so that the extremely broad signals start to disappear into the noise through coordination to Cu. Similar association processes in solution can again be proposed by means of the ESI mass spectra, which show peaks at higher mass numbers than the molecular weight in the solid state. For example, in the spectrum of the monomeric compound **6** the fragment $[\{P_3C_2Mes_2\}_4Cu_{11}I_6]^+$ is observed.

Due to its limited solubility, ^{31}P and ^{65}Cu MAS NMR spectra were acquired for compound **6**. Despite the rather high spinning frequency of 30 kHz, the $^{31}P\{^1H\}$ MAS NMR spectrum of **6** exhibits two broad featureless signals at 31.8 and 82.6 ppm with an integrated area ratio of about 2 : 1 in good agreement with the molecular structure of **6**. In comparison to reported data of copper-coordinated phosphorus cage compounds,[20] all peaks are noticeably shifted to lower ppm values, reminiscent of $Cu_3P_3I_2$ in which the polymeric phosphorus tube is coordinated by more flexible copper iodide ligands.[21] The presence of spinning sidebands in the ^{31}P MAS NMR spectrum indicates substantial ^{31}P chemical shift anisotropy typically observed in cases of locally distorted symmetry, e.g. imposed by the various ligands coordinated to phosphorus atoms. Any lineshape splitting due to ^{31}P-$^{63,65}Cu$ heteronuclear scalar interactions (*J*-couplings) could not be resolved at the applied magnetic fields (4.7 and 11.7 T), most likely owing to ^{31}P-$^{63,65}Cu$ residual dipolar couplings.[22] The ^{65}Cu MAS NMR spectrum of **6** is dominated by a Gaussian-shaped peak at 5.5 ppm, where the estimated quadrupolar coupling constant of $C_Q \approx 0.9$ MHz is comparable the coupling constant determined for purified solid copper(I) iodide, reflecting reasonable local symmetry such as tetrahedral coordination. Therefore, this peak is tentatively attributed to the copper atom coordinated to the single phosphorus atom rather than the P_2-‘dumbbell’. In contrast, the copper atoms comprising the highly distorted ‘crown’ motif are attributed to the weak featureless shoulders recognized in the region around -23 ppm.

Conclusions

In summary, we reported on an unexpected fragmentation of otherwise very stable phosphaferrocenes by reaction with Cu(I) halides. The observed splitting of $[Cp^*Fe(\eta^5\text{-}P_3C_2Mes_2)]$ (**1**) into a $[Cp^*Fe]^+$ and a $[P_3C_2Mes]^-$ unit can most likely attributed to the bulky mesityl ligands. While the $[Cp^*Fe]^+$ fragment reacts independently, the self-assembly process of the remaining phospholyl ligands and CuX (X = Cl, Br, I) leads to the formation of a large variety of coordination compounds, among them monomeric, dimeric as well as 1D and 2D polymeric aggregates. The obtained structural motifs represent novel ‘cages’ composed by P, Cu and X atoms (X = Cl, Br), a very seldom Cu_4I_4 ‘crown’ and a Cu_6I_6 ‘hexagram’ yet unknown for CuI systems. All obtained products show dynamic dissociation and association behaviour in solution, which alters the so far rather neglected 1,2,4-triphospholyl ligand to an interesting and attractive ligand in coordination chemistry. It remains to be investigated further whether the salt $K(P_3C_2Mes_2)$ can also be used as a building block in metallosupramolecular chemistry.

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Notes and references

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† In memory of Professor Kenneth Wade.

‡ Electronic Supplementary Information (ESI) available: Experimental Part, Crystallographic Data and additional figures. CCDC 1043724-1043731, see DOI: 10.1039/b000000x/

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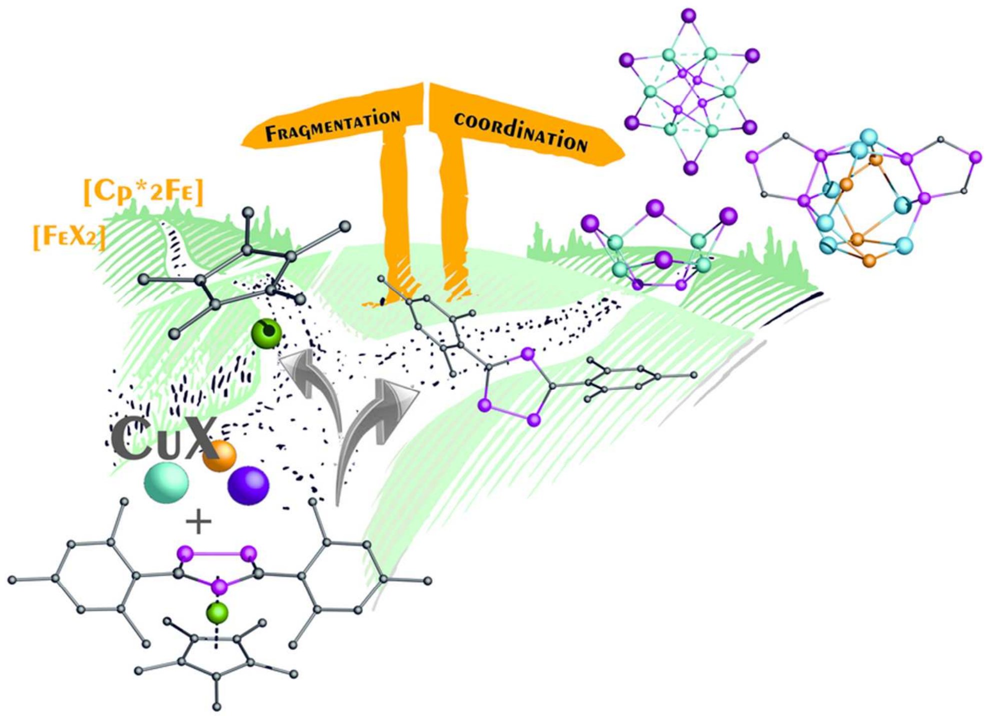

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An unusual fragmentation of a triphosphaferrocene is observed, when it is reacted with Cu(I) halides, as a result a large variety of different monomeric, dimeric and 1D and 2D polymeric coordination compounds are formed.