

Supramolecular Chemistry

Anionic Hosts for the Incorporation of Cationic Guests

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Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 70th birthday

Abstract: Pentaphosphaferrocene [Cp^{*}Fe(η⁵-P₅)] (**1a**) represents an excellent building block for the template-directed synthesis of spherical supramolecules. Here, the self-assembly of **1a** with Cu^I and Cu^{II} halides in the presence of the template complexes [FeCp₂][PF₆], [CoCp₂][PF₆] and [CoCp₂] is reported, testifying to the redox behavior of the formed supramolecules. The oxidation or reduction capacity of these reactive complexes does not inhibit their template impact and, for the first time, the cationic metallocene [CoCp₂]⁺ is

enclosed in unprecedented anionic organometallic hosts. Furthermore, the large variety of structural motifs, as icosahedral, trigonal antiprismatic, cuboidal and tetragonal antiprismatic arrangements of **1a** units are realized in the supramolecules [FeCp₂]₁₂@{**1a**}₁₂(CuBr)_{17,3} (**3**), [CoCp₂]₃⁺@{**1a**}₈Cu_{24,25}Br_{28,25}(CH₃CN)₆⁴⁻ (**4**), {[CoCp₂]₃⁺@{**1a**}₈(CuI)₂₈(CH₃CN)_{9,8}}]₃@{**1a**}₈Cu_{24,4}I_{26,4}(CH₃CN)₈²⁻ (**5**), and {[**1a**]₃{(**1a**)₂NH₃Cu₁₆I₁₀(CH₃CN)₇} (**6**), respectively.

Introduction

The self-assembly of DNA strands or enzyme-substrate-interactions demonstrates that supramolecular chemistry is an inherent feature of our daily life. During the last decades, this field of chemistry was successfully implemented in non-biological systems for the synthesis of large assemblies constructed by small building blocks through the self-assembly approach.^[1] Particularly intriguing is the synthesis of discrete spheres, which can act as containers for small molecules or ions.^[2] Within this area, coordinative bonds turned out to be a powerful tool for the rational design of novel cages or capsules, largely with di- or tridentate N, O or S donor ligands as connecting moieties.^[2,3]

Due to the lack of phosphorus donors in this chemistry, we have recently introduced pentaphosphaferrocenes [Cp^RFe(η⁵-P₅)] (**1a**: Cp^R = Cp^{*} = η⁵-C₅Me₅; **1b**: Cp^R = Cp^{Et} = η⁵-C₅Me₄Et;

1c: Cp^R = Cp^{Bn} = η⁵-C₅(CH₂C₆H₅)₅; **1d**: Cp^R = Cp^{BIG} = η⁵-C₅(4-*n*BuC₆H₄)₅) in combination with Cu^I salts (halides, triflates) for the formation of neutral nano-sized supramolecules, which show fullerene topology or beyond (Figure 1).^[4] With phosphorus as the donating element and possessing a fivefold symmetry, the *cyclo*-P₅ ligand in **1a–d** holds an outstanding position among the huge variety of building blocks. Notably, the obtained spheres are prime examples of template-directed syntheses, and the flexible coordination behavior of CuX (X = Cl, Br, I) as well as of the P₅ ring gives rise to the adaptability of this system. Accordingly, different sizes of the templates lead

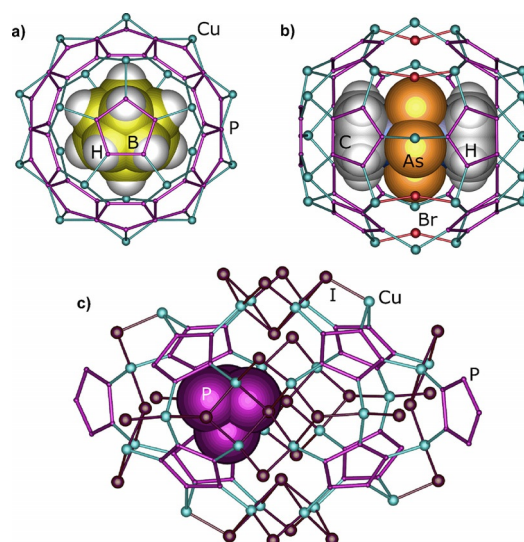


Figure 1. Selected scaffolds of spherical supramolecules composed by **1a**: a) 80-vertex scaffold incorporating *o*-carborane; b) 90-vertex scaffold incorporating [(CpCr)₂(μ,η⁵-As₅)]; c) 100-vertex scaffold incorporating a P₄ molecule (only one position of the disordered P₄ molecule is shown).

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to the formation of different-sized supramolecules exhibiting template-specific cavities (Figure 1).

Comparing the template properties, we not only succeeded in incorporating stable molecules as for instance ferrocene,^[4d] *o*-carborane^[4g] (Figure 1 a) and C₆₀^[4h] but were also able to stabilize otherwise very reactive and labile species such as white phosphorus and yellow arsenic by enclosure in a supramolecular host (Figure 1 c).^[4c] So far, all incorporated guests are neutral compounds, which fit in the neutral host environment. Hence, the question arises as to whether charged templates such as [FeCp₂]⁺ or [CoCp₂]⁺ can also be used for a template-directed formation of such supramolecules and whether this has an influence on the molecular structure of the host. Moreover, how the supramolecular system will respond to the introduction of a potentially redox active template is another question to be answered.

[MCp₂]⁺ cations have already been included into cavities of various organic cavitands such as calixarenes,^[5] thiacalixarenes,^[6] pillararenes,^[7] cyclodextrines^[8] and cucurbiturils.^[9] [CoCp₂]⁺ salts can also intercalate in some layered inorganic compounds, as for instance MoPS₃ or FePS₃,^[10] layered sulphides and selenides^[11] or mesoporous niobium oxide.^[12] To the best of our knowledge, there are no examples of the inclusion of [MCp₂]⁺ cations into cavities inside inorganic- or organometallic-based molecules because the redox properties usually prevent the inclusion.

Furthermore, even though labile species (e.g. As₄, P₄) turned out to be appropriate guests for pentaphosphaferrocene-derived supramolecules, they have never shown any reactivity towards the building blocks. Yet, particularly Cu in the oxidation state +1 is known for its redox activity. This fact sparked our interest regarding the introduction of reducing agents such as [CoCp₂] as a guest, which is also applicable to other host-guest systems.

Herein we report on the template-controlled self-assembly processes of [Cp*Fe(η⁵-P₅)] (**1 a**) and CuX (X = Br, I) and CuBr₂, respectively, in the presence of [FeCp₂][PF₆], [CoCp₂][PF₆] or [CoCp₂] as templates. Some self-assembly processes include the oxidation or reduction of the template and the subsequent incorporation of the cationic sandwich complex in an inorganic host for the first time. In this way, different supramolecules are obtained, some of which exhibit unprecedented scaffolds and shapes (Figure 2): [FeCp₂][Cp*Fe(η⁵-P₅)₁₂(CuBr)_{17.3}] (**3**), [CoCp₂]₃[CoCp₂]⁺@{[Cp*Fe(η⁵-P₅)₈Cu_{24.25}Br_{28.25}(CH₃CN)₆]⁴⁻} (**4**), {[Cp₂Co]⁺@{[Cp*Fe(η⁵-P₅)₈(Cu)₂₈(CH₃CN)_{9.8}}}{[Cp₂Co]⁺@{[Cp*Fe(η⁵-P₅)₈Cu_{24.4}Br_{26.4}(CH₃CN)₈]²⁻} (**5**), and {[Cp*Fe(η⁵-P₅)₃]{[Cp*Fe(η⁴-P₅)₂NH₃Cu₁₆Br₁₀(CH₃CN)₇}.3.9CH₃CN} (**6**).

Results and Discussion

Considering that ferrocene is known as an appropriate guest molecule for fullerene-like hosts,^[4a,d] the ferrocenium cation [FeCp₂]⁺ is the natural choice. When a solution of **1 a** in CH₂Cl₂ is layered with a solution of [FeCp₂][PF₆] and CuBr in acetonitrile, the formation of brown plates of the 2D polymer [(**1 a**)CuBr]_n^[13a] (**2 a**) and big dark blocks of [FeCp₂][Cp*Fe(η⁵-P₅)₁₂(CuBr)_{17.3}] (**3**) at the phase boundary is observed already

after one day. The X-ray structural analysis of **3** (trigonal, space group *R* $\bar{3}$) reveals a supramolecule constructed by 12 *cyclo*-P₅ ligands and 30 {Cu₂P₄} hexagons with a I_h-C₈₀ fullerene topology (Figure 2 a). Due to CuBr vacancies, the ideal scaffold of 20 CuBr units is reduced to an average of 17.3 moieties in **3**.^[14]

Such a partly vacant (80-*n*) vertex host molecule containing CuBr in its core was already observed once when *o*-carborane was encapsulated (Figure 1 a).^[15] Furthermore, the known Cl-derivative of this sphere is capable of the trapping of several templates such as *o*-carborane,^[4g] [CpCr(η⁵-As₅)]^[4d] and [FeCp₂]^[4d] although crystallizing in the cubic crystal system. Also in **3**, one molecule of the sandwich complex is enclosed within the cavity of the host. Surprisingly, neither [PF₆]⁻ nor an additional Br⁻ as counterion is present, obviously, the neutral metallocene is encapsulated. Diamagnetic ferrocene and the paramagnetic ferrocenium cation can easily be distinguished by EPR and NMR spectroscopy. The absence of a signal in the EPR spectrum and the presence of a signal in the ¹H NMR spectrum (δ = 4.16 ppm) give evidence of the incorporation of neutral ferrocene. The reduction of [FeCp₂]⁺ to [FeCp₂] is most probably enabled by oxidizing Cu⁺ to Cu²⁺, suggesting that an internal redox process occurred. To avoid this process, CuBr₂ was used and, interestingly the same product **3** was obtained showing no EPR signal of the ferrocenium cation, which points to the fact that pentaphosphaferrocene itself can also be redox-active, which was studied in the oxidation with a thianthrenium salt and the reduction with KH.^[16]

Hence, for the incorporation of a cation, a more stable complex might be required. Therefore, the 18-valence-electron complex [CoCp₂][PF₆] was used as a template. Applying the same conditions as before, the formation of brown plates of the polymer [(**1 a**)CuBr]_n (**2 a**)^[13a] as the minor product and small reddish rhombohedra of [CoCp₂]₃[CoCp₂]⁺@{[Cp*Fe(η⁵-P₅)₈Cu_{24.25}Br_{28.25}(CH₃CN)₆]⁴⁻} (**4**) as the major product can be observed after a few days. The X-ray structural analysis of **4** reveals an unprecedented spherical supramolecule, which does not follow the fullerene topology. It contains eight molecules of **1 a**, which are arranged by the vertices of a square antiprism (Figure 2 b). This overall number of P₅ units in the sphere is exceptional because fullerene-like species usually contain 12 *cyclo*-P₅ ligands.^[4] There is only one CuBr-containing supramolecule known with 24 units of **1 a**,^[17] and another one, however CuI-based, with 10 P₅ rings, possessing a cube-like scaffold (Figure 1 c).^[4c]

The CuBr scaffold in **4** consists of a severely disordered middle framework with the sum composition of Cu_{16.25}Br_{18.25}(CH₃CN)₆, which is completed from above and below by bowl-like {Cu₄Br₃}⁻ fragments (Figure 3 a). The analogous {Cu₄I₃}⁻ bowl is also a part of the scaffold of a CuI-containing supramolecule (Figure 1 c).^[4c,18] The middle part can further be divided into anionic {Cu₂(μ₃-Br)Br₂}⁻, neutral {Cu₂(μ₃-Br)Br(CH₃CN)} and cationic {Cu₂(μ₃-Br)(CH₃CN)₂}⁺ fragments with partly occupied Cu and Br positions.^[19] In total (middle part and two 'bowls'), a sum formula of {[Cp*Fe(η⁵-P₅)₈Cu_{24.25}Br_{28.25}(CH₃CN)₆]⁴⁻} results for the inorganic host. The negative charge is balanced by four [CoCp₂]⁺ cations. Three of them are located in the outer sphere; the fourth one fits exact-

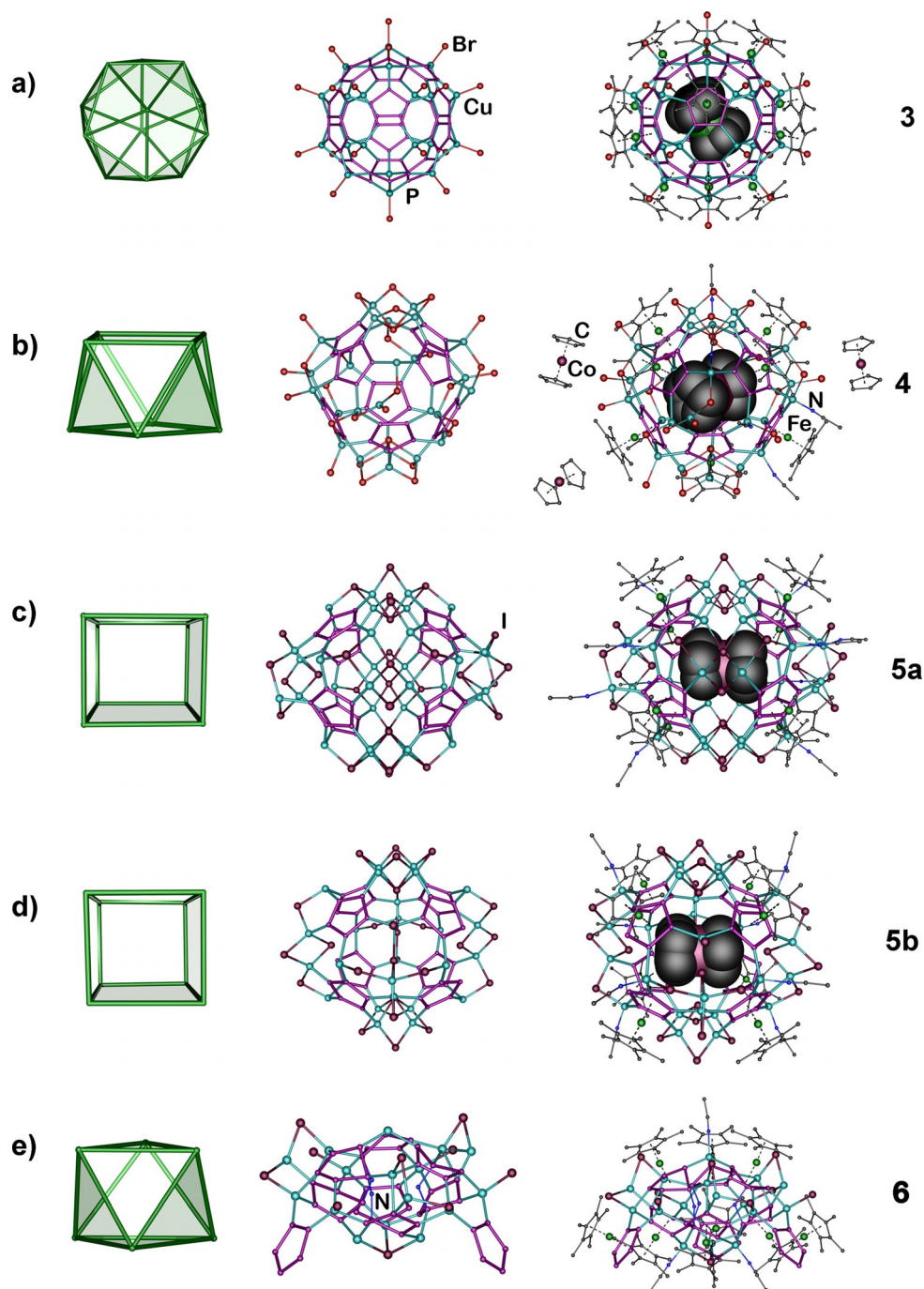


Figure 2. Schematic view of scaffolds (left), scaffolds (middle) and molecular structures (right) of the obtained supramolecules **3–6** with $[\text{FeCp}_2]/[\text{CoCp}_2]/[\text{CoCp}_2][\text{PF}_6]$ as template. Hydrogen atoms, minor parts of disorder and solvent molecules are omitted for clarity. Incorporated templates are displayed in a space-filling model.

ly into the cavity of the supramolecule (Figure 2b). Hence, the building blocks **1a** and CuBr adapt to the cationic template by forming an unprecedented anionic host, which displays the first negatively charged inorganic assembly of this series, here incorporating $[\text{Cp}_2\text{M}]^+$.

Encouraged by this result, we became interested in the investigation of the potential of the neutral moiety $[\text{CoCp}_2]$ as a template. For this purpose, a dark green solution of **1a** and CoCp_2 (molar ratio **1a**: CoCp_2 = 3:1) in CH_2Cl_2 is layered over a solution of CuBr in CH_3CN . In doing so, the formation of a met-

allic mirror was observed, most likely of Cu^0 . Nonetheless, after some days, in addition to the formation of brown plates of the 2D polymer $[(\mathbf{1a})\text{CuBr}]_n$ (**2a**),^[13a] small red plates are formed. The X-ray structure analysis of these plates reveals the same charged sphere **4**, as that isolated when using $[\text{CoCp}_2][\text{PF}_6]$. Having 19 valence electrons, $[\text{CoCp}_2]$ serves as a strong and widely used reducing agent. Hence, Cu^+ is reduced by the metallocene to give elemental Cu and the formed $[\text{CoCp}_2]^+$ is again incorporated to give **4** in 51% crystalline yield. To avoid the loss of copper during this reaction, CuBr was exchanged

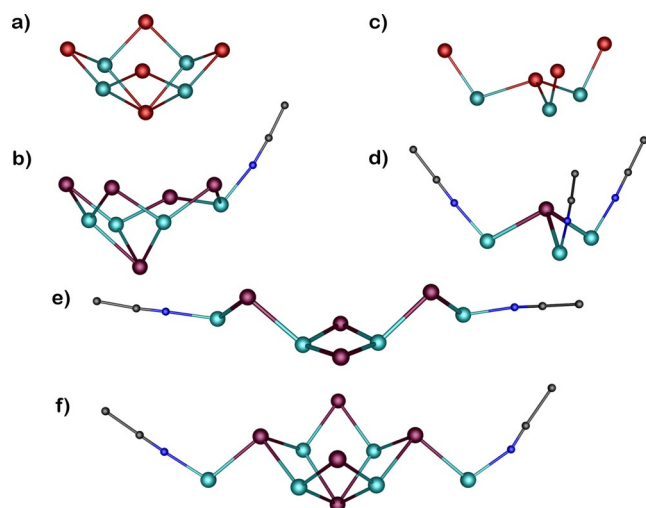


Figure 3. Typical fragments in CuX frameworks (X = Br, I): Bowl-like fragments (a) $\{Cu_4Br_3\}^-$ in the scaffold of **4** and (b) $\{Cu_4I_5(CH_3CN)\}$ in **5a**; caps (c) $\{Cu_3Br_4\}^-$ in **4** and (d) $\{Cu_3Br(CH_3CN)_3\}^{2-}$ in **6**; and $\{Cu_4I_4(CH_3CN)_2\}$ and $\{Cu_6I_5(CH_3CN)_2\}^-$ fragments in **5a** and **5b**.

for its corresponding Cu^{II} salt. And, in fact, the self-assembly process leads again to the formation of small plates of **4** after the reduction of Cu^{II} to Cu^I . Unfortunately, the yield could not be increased by this method because the polymeric by-product **2a**^[13a] is also formed during this reaction. These results nicely demonstrate the suitability of $[CoCp_2]^+$ as a template because the novel supramolecule **4** is formed in all three systems: **1a**/ $[CoCp_2]$ / PF_6^- / $CuBr$, **1a**/ $[CoCp_2]$ / $CuBr$ and **1a**/ $[CoCp_2]$ / $CuBr_2$.

Moreover, if CuI is used in the reaction with **1a** in the presence of $[Cp_2Co]$, brown plates of the polymer $[(1a)Cu]_n$ (**2b**)^[13a] and small red prisms of $\{[Cp_2Co]^+@[(Cp^*Fe(\eta^5-P_5))_8\{Cu_4I_5\}_2\{Cu_2I_4\}_2\{Cu_4I_5(CH_3CN)\}]_{1,8}\{Cu(CH_3CN)\}_8]\} [Cp_2Co]^+ @[(Cp^*Fe(\eta^5-P_5))_8\{Cu_4I_5\}_2\{Cu_2I_4\}_4\{CuI\}]_{0,4}\{Cu(CH_3CN)\}_8\}^{2-}$ (**5**) are formed. Compound **5** crystallizes in the monoclinic space group $P2_1/c$. Its structure reveals two different supramolecules, the neutral host sphere $[(Cp^*Fe(\eta^5-P_5))_8\{Cu_4I_5\}_2\{Cu_2I_4\}_2\{Cu_4I_5(CH_3CN)\}]_{1,8}\{Cu(CH_3CN)\}_8$ (**5a**) and the anionic host supramolecule $[(Cp^*Fe(\eta^5-P_5))_8\{Cu_4I_5\}_2\{Cu_2I_4\}_4\{CuI\}]_{0,4}\{Cu(CH_3CN)\}_8\}^{2-}$ (**5b**) (Figure 2c,d). Both of them consist of eight units of **1a**, four of them in a 1,2,3,4,5- and the other four in a 1,2,3,4- coordination mode of the *cyclo*- P_5 ligand. The extended CuI framework can be explained as a combination of different fragments. In **5b**, four $\{Cu_2I_4\}^{2-}$ fragments appear as two different structural isomers linked by additional $\{Cu(CH_3CN)\}^+$ groups and partly occupied $\{CuI\}$ units (Figure 3e). From above and below, the sphere is completed by bowl-like $\{Cu_4I_5\}^-$ fragments as observed in **4** and in a supramolecule containing ten *cyclo*- P_5 units, respectively (also see Figure 1c).^[4c] Hence, for the host **5b**, the sum formula $[(1a)_8Cu_{24}I_{41}Cu_4(CH_3CN)]_8\}^{2-}$ with a 91-vertex scaffold results (Figure 2d). Its elongated cavity ranges from 4.9 Å in width and 6.7 Å in length and is therefore perfectly suitable for the encapsulation of a cobaltocenium cation, which has a length of 6.6 Å. This leads to the monoanionic host-guest supramolecular complex $[(CoCp_2)^+@5b]^-$. In **5a**, instead of some $\{Cu_2I_4\}^{2-}$

fragments, a bowl-like $\{Cu_4I_5\}^-$ and $\{Cu_4I_5(CH_3CN)\}$ fragments (Figure 3b) prevail to construct a neutral 96-vertex scaffold of the sum formula $[(1a)_8(CuI)_{28}(CH_3CN)_{9,8}]$ (Figure 2c). Its inner diameter (4.9 Å × 7.1 Å) is once more large enough for the encapsulation of a small molecule. Hence, one $[CoCp_2]^+$ is incorporated resulting in a monocationic host-guest complex $[(CoCp_2)^+@5a]^+$. Thus, it balances the negative charge of $[(CoCp_2)^+@5b]^-$. Compound **5** can therefore be described as a unique supramolecular ion pair $[(CoCp_2)^+@5a]^+[(CoCp_2)^+@5b]^-$. The outer diameter reaches values of 2.67 nm for **5b** and 2.99 nm for **5a**, respectively.^[20] The dianionic **5b** host is smaller than the neutral **5a** due to the difference in the CuI scaffold: In **5b**, the shortest bridge between neighbouring *cyclo*- P_5 ligands is a single Cu atom coordinating P atoms in 1,2-positions. In **5a**, the corresponding *cyclo*- P_5 ligands are linked by Cu and longer Cu_2I -bridges, which leads to a longer size of two opposite faces of the underlying cube in the scaffold of **5a**. For comparison, the 80- and 90-vertex nanoballs (Figure 1a,b) have a size of 2.2 nm, whereas fullerene C_{60} amounts to only 0.7 nm.^[20]

The host-guest interactions in **4** and **5** are different in comparison to those in **3** (Figure 2). In the latter, relatively weak π - π stacking took place between both Cp ligands of the $[FeCp_2]$ guest and two opposite *cyclo*- P_5 ligands of the host (interplanar distances 3.95–4.15 Å). In the complexes **4** and **5**, no stacking interactions are observed with $[Cp_2Co]^+$, which is reasonable for the supramolecule **4** with its antiprismatic and, hence, non-parallel orientation of the P_5 rings (Figure S8 in the Supporting Information). In **5**, there is no π - π stacking even despite a parallel orientation of the *cyclo*- P_5 rings of both the neutral and the anionic hosts. The cube-like arrangement of the *cyclo*- P_5 rings would allow both Cp ligands of the MCp_2 to be involved in the π interactions. The host cavity sizes would still be suitable with their *cyclo*- P_5 ...*cyclo*- P_5 distances [cf. average of 11.34 Å (**3**), 11.38 Å (**5b**) and 11.86 Å (**5a**)]. Yet, the parallel arrangement of the P_5 rings on the inner surface of the cavity might be not good enough, because they are not exactly opposite. For this reason, in the case of both hosts in **5**, only slipped stacking with the guest metallocene molecules could have taken place. Most probably, a face-to-face stacking as in **3** is more favourable than the slipped one. Therefore, the guest molecule chooses the orientation in the cavity, where only numerous $H\cdots P$ and $H\cdots X$ van der Waals contacts are formed with the host molecules **4** or **5**. The shortest $H\cdots P$ (2.88–2.92 Å) and $H\cdots Br$ contacts (2.94–2.95 Å) are all normal van der Waals contacts. In **5**, only $H\cdots I$ (2.79–3.07 Å) contacts are shortened with respect to van der Waals radii, and the $H\cdots P$ contacts are all longer than 3 Å. To investigate the possible ordering of the $[CoCp_2]^+$ cationic host, an additional X-ray diffraction experiment for **4** was measured at 10 K at the DESY PETRA III synchrotron (beamline P11).^[21] The experiment showed that no ordering takes place and therefore no specific interactions are responsible for the host-guest interactions.

In the presence of the $[CoCp_2]^+$ cation, a number of iodocuprates of oligomeric (up to $[Cu_6I_{11}]^{5-}$) and 2D polymeric structures are known to be formed in acetonitrile solutions.^[22] When synthesizing **5**, no iodocuprates were observed, but

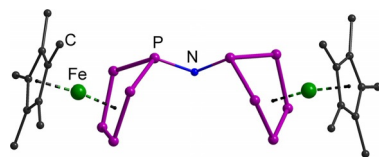


Figure 4. Envelope conformation of six *cyclo-P*₅ rings in **6**.

from time to time, black plates of $[\{\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)\}_3\{\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5)_2\text{NH}\}]_3\text{Cu}_{16}\text{I}_{10}(\text{CH}_3\text{CN})_7\cdot 3.9\text{CH}_3\text{CN}$ (**6**) could be obtained. Compound **6** crystallizes in the monoclinic space group $P2_1/c$ and its X-ray structure analysis shows a further unprecedented supramolecule of a hemispherical, lens-like shape (Figure 2e). It contains nine pentaphosphaferrocene moieties, with six of them showing an envelope conformation of the P_5 ring. The “out-of-plane” phosphorus atom also bears a substituent, which is attributed to a NH group.^[23] The nitrogen atom bridges two neighbouring $[\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5)]$ units to give three $[\{\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5)\}_2\text{NH}]^{2-}$ moieties per supramolecule (Figure 4). Similar complexes were obtained in our group as a result of the nucleophilic attack of **1a** by NH_2^- , an intermediate complex $[\{\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5)\}_2\text{NH}]^{2-}$ detected by ^{31}P NMR spectroscopy and a final product $[\{\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5)\}_2\text{N}]^{3-}$, the latter being also characterized by X-ray structure analysis.^[24] The $[\{\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5)\}_2\text{NH}]^{2-}$ units in **6** and the trianion $[\{\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5)\}_2\text{N}]^{3-}$ display a similar envelope conformation of the *cyclo-P*₅ ligand and reasonably elongated P–N bond lengths when protonation is taken into account ($[\{\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5)\}_2\text{N}]^{3-}$: 1.688(3)–1.693(3) and **6**: 1.697(17)–1.736(9) Å). In **6**, these bent P_5 rings still show a 1,2,3,4,5-coordination mode, whereas the remaining three units of **1a** bearing planar *cyclo-P*₅ ligands show a 1,2-coordination mode. The scaffold furthermore contains 16 tetrahedrally coordinated Cu^+ and 10 I^- ions, which are either terminal or bridging (μ_2 or μ_3). In total, the supramolecule is neutral (3 $[\{\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5)\}_2\text{NH}]^{2-}$, 10 I^- , 16 Cu^+). Due to the interconnected *cyclo-P*₅ ligands, compound **6** does not provide any accessible cavity, hence no encapsulation of the template is observed. The outer size of the supramolecule amounts to 1.65×2.48 nm.^[20] Unfortunately, all attempts to isolate **6** in significant amounts failed.^[24]

All obtained supramolecular compounds **3–6** are insoluble in common solvents as *n*-hexane, toluene, Et_2O and THF. In some cases, however, they show a very low solubility in CH_3CN , CH_2Cl_2 or mixtures of these solvents, enabling a mass spectrometric characterization,^[19] with fragments of even up to $[\{\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)\}_3\text{Cu}_7\text{Br}_6]^+$ (at $m/z = 1962.3$) for **3** appearing in the corresponding ESI spectra. Furthermore, this method is also well-suited for the detection of the template, although no conclusion about its charge can be made. In the cationic ESI mass spectrum of **4** and **5**, an exemplary peak at $m/z = 188.9$ corresponding to $[\text{CoCp}_2]^+$ is observed.

In addition, all products show solubility in pyridine, accompanied by the fragmentation of the host and thus the release of the guest. This is evidenced by both the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, which only show signals corresponding to the free **1a**. As an example, for dissolved crystals of **3**, a sharp singlet at $\delta = 143.5$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (*cyclo-P*₅) and a sin-

glet at $\delta = 1.34$ ppm in the ^1H NMR spectrum (Cp^* ligand) are obtained corresponding to the free **1a**,^[19] a consequence of which is the release of the template, which also can be detected by NMR or EPR spectroscopy as well as mass spectrometry. Thus, in the ^1H NMR spectrum of **3**, in pyridine, a singlet at $\delta = 4.16$ ppm is assigned to the Cp ligands of ferrocene (literature:^[25] $\delta = 4.04$ ppm in cyclohexane- d_{12}). In the respective EPR spectra of **3**, **4** and **5** in pyridine solution, no signal can be detected, which is in agreement with the presence of the neutral 18 VE complex $[\text{FeCp}_2]$ in **3** as well as of the cationic 18 VE complex $[\text{CoCp}_2]^+$ in **4** and **5**.

Conclusion

For the first time, the formation of supramolecules in the presence of redox-active agents was demonstrated. Even the presence of the reducing agent $[\text{CoCp}_2]$ as well as of the oxidant $[\text{FeCp}_2][\text{PF}_6]$ does not inhibit the formation of supramolecules based on pentaphosphaferrocene **1a** and CuX ($X = \text{Br}, \text{I}$). In contrast, their respective oxidation and reduction are accompanied by their incorporation in the in situ formed supramolecular hosts. In the presence of $[\text{FeCp}_2][\text{PF}_6]$, the sphere **3** of the $I_h\text{-C}_{80}$ topology is formed consisting of 12 fragments of **1a**. According to EPR data, the sphere is templated by neutral $[\text{FeCp}_2]$ guest, a product of the reduction of the $[\text{FeCp}_2]^+$. In contrast, under similar conditions, $[\text{CoCp}_2]$ is oxidized by Cu^+ now forming the charged template $[\text{CoCp}_2]^+$. This resulting cationic organometallic complex was successfully included into three different supramolecules **4**, **5a** and **5b**, possessing novel topologies. It was also proved that the direct synthesis starting from the $[\text{CoCp}_2][\text{PF}_6]$ salt results in the same products **4**, **5a** and **5b**. Therefore, this approach allowed us to isolate and structurally characterize both neutral and anionic supramolecules with unprecedented scaffolds that differ in shape, the number of **1a** moieties and the halide used. In the fourfold positively charged supramolecule **4**, eight units of **1a** form a square antiprism, whereas in **5**, they are arranged in two diverse cubes, one being neutral (**5a**), the other being twofold negatively charged (**5b**). These host–guest assemblies with the cuboidal scaffolds **5** form a unique ion pair $[(\text{CoCp}_2)^+@5\mathbf{a}]^+ [(\text{CoCp}_2)^+@5\mathbf{b}]^-$. Remarkably, the host–guest complexes **4** and **5** display the first inorganic-based spheres incorporating $[\text{CoCp}_2]^+$.

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Conflict of interest

The authors declare no conflict of interest.

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- [1] a) S. I. Stupp, L. C. Palmer, *Chem. Mater.* **2014**, *26*, 507–518; b) N. Lanigan, X. Wang, *Chem. Commun.* **2013**, *49*, 8133–8144; c) R. W. Saalfrank, A. Scheurer, *Top. Curr. Chem.* **2011**, *319*, 125–170; d) S. J. Dalgarno, *Annu. Rep. Prog. Chem.* **2010**, *106*, 197–215; e) M. Mastalerz, *Angew. Chem. Int. Ed.* **2010**, *49*, 5042–5053; *Angew. Chem.* **2010**, *122*, 5164–5175; f) T. H. Rehm, C. Schmuck, *Chem. Soc. Rev.* **2010**, *39*, 3597–3611; g) J.-M. Lehn, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4763–4768; h) F. A. Cotton, C. Lin, C. A. Murillo, *Acc. Chem. Res.* **2001**, *34*, 759–771; i) D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka, M. Fujita, *Nature* **2016**, *540*, 563–566.
- [2] a) A. Müller, P. Gouzerh, *Chem. Eur. J.* **2014**, *20*, 4862–4873; b) S. Mukherjee, P. S. Mukherjee, *Chem. Commun.* **2014**, *50*, 2239–2248; c) W. Meng, J. K. Clegg, J. R. Nitschke, *Angew. Chem. Int. Ed.* **2012**, *51*, 1881–1884; *Angew. Chem.* **2012**, *124*, 1917–1920; d) Z. Laughrey, B. C. Gibb, *Chem. Soc. Rev.* **2011**, *40*, 363–386; e) B. Breiner, J. K. Clegg, J. R. Nitschke, *Chem. Sci.* **2011**, *2*, 51–56; f) Y. Inokuma, M. Kawano, M. Fujita, *Nat. Chem.* **2011**, *3*, 349–358; g) P. Jin, S. J. Dalgarno, J. L. Atwood, *Coord. Chem. Rev.* **2010**, *254*, 1760–1768; h) M. Yoshizawa, J. K. Klosterman, M. Fujita, *Angew. Chem. Int. Ed.* **2009**, *48*, 3418–3438; *Angew. Chem.* **2009**, *121*, 3470–3490; i) T. S. Koblenz, J. Wassenaar, J. N. H. Reek, *Chem. Soc. Rev.* **2008**, *37*, 247–262; j) S. J. Dalgarno, N. P. Power, J. L. Atwood, *Coord. Chem. Rev.* **2008**, *252*, 825–841; k) C. Schmuck, *Angew. Chem. Int. Ed.* **2007**, *46*, 5830–5833; *Angew. Chem.* **2007**, *119*, 5932–5935; l) B. J. Holliday, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2001**, *40*, 2022–2043; *Angew. Chem.* **2001**, *113*, 2076–2097; m) T. Heinz, D. M. Rudkevich, J. Rebek, Jr., *Nature* **1998**, *394*, 764–766.
- [3] a) N. J. Young, B. P. Hay, *Chem. Commun.* **2013**, *49*, 1354–1379; b) L. F. Lindoy, K.-M. Park, S. S. Lee, *Chem. Soc. Rev.* **2013**, *42*, 1713–1727; c) M. Schmidtdorf, T. Pape, F. E. Hahn, *Angew. Chem. Int. Ed.* **2012**, *51*, 2195–2219; *Angew. Chem.* **2012**, *124*, 2238–2241; d) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972–983.
- [4] a) F. Dielmann, M. Fleischmann, C. Heindl, E. Peresyckina, A. V. Virovets, R. M. Gschwind, M. Scheer, *Chem. Eur. J.* **2015**, *21*, 6208; b) S. Heindl, E. Peresyckina, J. Sutter, M. Scheer, *Angew. Chem. Int. Ed.* **2015**, *54*, 13431–13435; *Angew. Chem.* **2015**, *127*, 13631–13635; c) C. Schwarzmaier, A. Schindler, C. Heindl, S. Scheuermayer, E. Peresyckina, A. V. Virovets, M. Neumeier, R. Gschwind, M. Scheer, *Angew. Chem. Int. Ed.* **2013**, *52*, 10896–10899; *Angew. Chem.* **2013**, *125*, 11097–11100; d) A. Schindler, C. Heindl, G. Balazs, C. Groeger, A. V. Virovets, E. V. Peresyckina, M. Scheer, *Chem. Eur. J.* **2012**, *18*, 829–835; e) S. Welsch, C. Groeger, M. Sierka, M. Scheer, *Angew. Chem. Int. Ed.* **2011**, *50*, 1435–1438; *Angew. Chem.* **2011**, *123*, 1471–1474; f) M. Scheer, A. Schindler, J. Bai, B. P. Johnson, R. Merkle, R. Winter, A. V. Virovets, E. Peresyckina, V. A. Blatov, M. Sierka, H. Eckert, *Chem. Eur. J.* **2010**, *16*, 2092–2107; g) M. Scheer, A. Schindler, C. Gröger, A. V. Virovets, E. Peresyckina, *Angew. Chem. Int. Ed.* **2009**, *48*, 5046–5049; *Angew. Chem.* **2009**, *121*, 5148–5151; h) M. Scheer, A. Schindler, R. Merkle, B. P. Johnson, M. Linseis, R. Winter, C. E. Anson, A. V. Virovets, *J. Am. Chem. Soc.* **2007**, *129*, 13386–13387; i) M. Scheer, J. Bai, B. P. Johnson, R. Merkle, A. V. Virovets, C. E. Anson, *Eur. J. Inorg. Chem.* **2005**, *20*, 4023–4026; j) J. Bai, A. V. Virovets, M. Scheer, *Science* **2003**, *300*, 781–783; k) F. Dielmann, E. Peresyckina, B. Krämer, F. Hastreiter, B. P. Johnson, M. Zabel, C. Heindl, M. Scheer, *Angew. Chem. Int. Ed.* **2016**, *55*, 14833–14837; *Angew. Chem.* **2016**, *128*, 15053–15058; l) C. Heindl, E. Peresyckina, A. V. Virovets, I. S. Bushmarinov, M. G. Medvedev, B. Krämer, B. Dittrich, M. Scheer, *Angew. Chem. Int. Ed.* **2017**, *56*, 13237–13243.
- [5] a) A. V. Mossine, H. Kumari, D. A. Fowler, A. K. Maerz, S. R. Kline, C. L. Barnes, J. L. Atwood, *Isr. J. Chem.* **2011**, *51*, 840–842; b) V. Rudzevich, O. Kasyan, A. Drapailo, M. Bolte, D. Schollmeyer, V. Böhmer, *Chem. Asian J.* **2010**, *5*, 1347–1355; c) P. D. Beer, A. D. Keefe, A. M. Z. Slawin, D. J. Williams, *J. Chem. Soc. Dalton Trans.* **1990**, 3675–3682; d) Y. Wang, A. E. Kaifer, *Chem. Commun.* **1998**, 1457–1458.
- [6] L. Frish, M. O. Vysotsky, V. Boehmer, Y. Cohen, *Org. Biomol. Chem.* **2003**, *1*, 2011–2014.
- [7] W. Xia, X.-Y. Hu, Y. Chen, C. Lin, L. Wang, *Chem. Commun.* **2013**, *49*, 5085–5087.
- [8] a) A. U. Moozyckine, J. L. Bookham, M. E. Deary, D. M. Davies, *J. Chem. Soc. Perkin Trans. 1* **2001**, *2*, 1858–1862; b) B. Klingert, G. Rihs, *J. Chem. Soc. Dalton Trans.* **1991**, 2749–2760.
- [9] a) A. E. Kaifer, *Acc. Chem. Res.* **2014**, *47*, 2160–2167; b) S. Gadde, A. E. Kaifer, *Curr. Org. Chem.* **2011**, *15*, 27–38.
- [10] a) H. Sakai, T. Yamazaki, N. Machida, T. Shigematsu, S. Nasu, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **2000**, *341*, 105–110; b) J. S. O. Evans, D. O'Hare, R. Clement, *J. Am. Chem. Soc.* **1995**, *117*, 4595–4606.
- [11] a) A. N. Titov, O. N. Suvorova, S. Y. Ketkov, S. G. Titova, A. I. Merentsov, *Phys. Solid State* **2006**, *48*, 1466–1471; b) L. Hernan, J. Morales, L. Sanchez, J. Santos, E. Rodriguez-Castellon, J. L. Martinez, *Chem. Mater.* **2000**, *12*, 3792–3797; c) A. Ibarz, E. Ruiz, S. Alvarez, *J. Chem. Soc. Dalton Trans.* **2000**, 1463–1467.
- [12] S. Murray, M. Trudeau, D. M. Antonelli, *Adv. Mater.* **2000**, *12*, 1339–1342.
- [13] a) J. Bai, A. V. Virovets, M. Scheer, *Angew. Chem. Int. Ed.* **2002**, *41*, 1737–1740; *Angew. Chem.* **2002**, *114*, 1808–1811; b) F. Dielmann, A. Schindler, S. Scheuermayer, J. Bai, R. Merkle, M. Zabel, A. V. Virovets, E. V. Peresyckina, G. Brunklaus, H. Eckert, M. Scheer, *Chem. Eur. J.* **2012**, *18*, 1168–1179.
- [14] For a more detailed discussion of these scaffold vacancies see: ref. [4a] and E. Peresyckina, C. Heindl, A. Virovets, M. Scheer, *Structure and Bonding* **2016**, *174*, 321–373.
- [15] E. V. Peresyckina, C. Heindl, A. Schindler, M. Bodensteiner, A. V. Virovets, M. Scheer, *Z. Kristallogr.* **2014**, *229*, 735–740.
- [16] a) M. V. Butovskiy, G. Balázs, M. Bodensteiner, E. V. Peresyckina, A. V. Virovets, J. Sutter, M. Scheer, *Angew. Chem. Int. Ed.* **2013**, *52*, 2972–2976; *Angew. Chem.* **2013**, *125*, 3045–3049; b) E. Mädl, M. V. Butovskii, G. Balázs, E. V. Peresyckina, A. V. Virovets, M. Seidl, M. Scheer, *Angew. Chem. Int. Ed.* **2014**, *53*, 7643–7646; *Angew. Chem.* **2014**, *126*, 7774–7777.
- [17] C. Heindl, E. V. Peresyckina, A. V. Virovets, W. Kremer, M. Scheer, *J. Am. Chem. Soc.* **2015**, *137*, 10938–10941.
- [18] X. H. Wu, J.-T. Guan, G.-A. Yu, Yu.-H. Yang, B. Zhang, X.-G. Meng, S.-H. Liu, *J. Coord. Chem.* **2009**, *62*, 3930–3939.
- [19] See the Supporting Information for details.
- [20] The outer diameter is taken as the largest distance between the farthest atoms, plus twice the van der Waals radius for the respective atom (e.g., H: 1.2 Å). The inner diameters of the cavities were calculated as geometrically opposing atomic distances, minus the van der Waals radii of the respective atoms (e.g., P: 1.80 Å, Cu: 1.40 Å).
- [21] A. Burkhardt, T. Pakendorf, B. Reime, J. Meyer, P. Fischer, N. Stübe, S. Panneerselvam, O. Lorbeer, K. Stachnik, M. Warmer, P. Rödig, D. Göries, A. Meents, *Eur. Phys. J. Plus* **2016**, *131*, 56–64.
- [22] a) H. Hartl, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 927–928; *Angew. Chem.* **1987**, *99*, 925–927; b) H. Hartl, I. Brudgam, *Z. Naturforsch. B* **1989**, *44*, 936–941.
- [23] The nature of the bridging atom has been assigned to a nitrogen atom rather than to an oxygen atom due to the convincing structural similarity to the known complex $[\text{Na}_3(\text{dme})_3][\{\text{Cp}^*\text{Fe}(\eta^1\text{-P}_3)_2\text{N}\}]$ and the striking difference to $[\text{Na}_2(\text{dme})_3][\{\text{Cp}^*\text{Fe}(\eta^1\text{-P}_3)_2\text{O}\}]$ (7); see ref. [16b] and Supporting Information for more details.
- [24] All attempts to isolate **6** in significant amounts failed, even when acetonitrile was used without special purification to allow organic amides into the system. Moreover, the direct reaction in the presence of NaNH_2 did not give **6**, probably due to the low solubility of the sodium amide. To check the possibility of having oxygen as a bridging atom, additional H_2O was added to the solvent or traces of air were let into the Schlenk tube. No product **6** was formed in this case either, but various polymeric products **2b** were identified; see ref. [13a,b].
- [25] L. Phillips, F. Separovic, M. J. Aroney, *New J. Chem.* **2003**, *27*, 381–386.

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