The Missing Parent Compound \([(\text{C}_5\text{H}_5)\text{Fe}(\eta^5-\text{P}_5)]\): Synthesis, Characterization, Coordination Behavior and Encapsulation

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Dedicated to Prof. Otto J. Scherer in honor for his seminal achievements in pentaphosphaferrocene chemistry

Abstract: The so far missing parent compound of the large family of pentaphosphaferroenes \([\text{CpFe}(\eta^5-\text{P}_5)]\) (1b) was synthesized by the thermolysis of \([\text{CpFe(OC)}_2]_n\) with \(\text{P}_5\) using the very high-boiling solvent diisopropylbenzene. It was comprehensively characterized by, inter alia, NMR spectroscopy, single crystal X-ray structure analysis, cyclic voltammetry and DFT computations. Moreover, its coordination behavior towards \(\text{Cu}^+\) halides was explored, revealing the unprecedented 2D polymeric networks \([\text{CpFe}(\eta^5-\text{P}_5)]\text{Cu}_2(\mu-X)_3\)_\(n\), (2a: \(X = \text{Cl}\), 2b: \(X = \text{Br}\)) and \([\text{CpFe}(\eta^5-\text{P}_5)]\text{Cu}(\mu-I)_n\) (3) and even the first cyclo-\(\text{P}_5\)-containing 3D coordination polymer \([\text{CpFe}(\eta^5-\text{P}_5)]\text{Cu}(\mu-I)_n\) (4). The sandwich complex 1b can also be incorporated in nano-sized supramolecules based on \([\text{Cp*Fe}(\eta^5-\text{P}_5)]\) (1a) and \(\text{CuX}\) (\(X = \text{Cl}, \text{Br}, \text{I}\)): \([\text{Cp*Fe}(\eta^5-\text{P}_5)]\)_{\(n\}}[\text{Cu}(\mu-I)]_{\(n\}}\) (5a: \(X = \text{Cl}\), \(n = 2.4\); 5b: \(X = \text{Br}\), \(n = 2.4\); 5c: \(X = \text{I}\), \(n = 0.95\)). Thereby, the formation of the \(\text{Cu}\)-containing fullerene-like sphere 5c is found for the first time.

Introduction

The establishment of organometallic chemistry as a distinct field of chemistry is—to a large extent—owed to the discovery and structure determination of the ferrocene molecule \([\text{Fe}(\eta^5-\text{C}_5\text{H}_5)]\) in 1951,[1] for which E. O. Fischer and G. Wilkinson were awarded the Noble Prize in 1973.[2] Beside their application as a reference redox system \((\text{Fc}/\text{Fc}^+)^{[3]}\), ferrocene derivatives play an important role for example, in asymmetric catalysis,[4] polymer chemistry[5] and for magnetic materials.[6] These derivatives can not only be varied in their functionalization pattern, but also in the substitution of the methine moieties of the \(\text{C}_5\text{H}_5\) group by isolobal heteroatoms. Since a \(\text{P}\) atom is isolobal to a \(\text{CH}\) fragment, the introduction of phosphorus atoms into the cyclopentadienyl ligand affords the class of phosphoferrocenes.[7] Among them, the \(\text{Cp}^\ast\)-substituted pentaphosphaferrocene \([\text{Cp*Fe}(\eta^5-\text{P}_5)]\) \((\text{Cp}^\ast = \text{C}_5\text{Me}_5)\) (1a), containing a cyclo-\(\text{P}_5\) ligand, is of special interest. First published in 1987 by Scherer et al.,[8] it shows a remarkable similarity to ferrocene, since it was possible to oxidize, reduce and substitute on the cyclo-\(\text{P}_5\) ring.[9] Moreover, it has become an important building block not only in organometallic,[10] but also in coordination and supramolecular chemistry especially for the formation of 1D and 2D polymers.[11]

Of special interest is its ability to act as a building block for the formation of spherical supramolecules with fullerene topology by a self-assembly process with \(\text{CuX}\) (\(X = \text{Cl}, \text{Br}\)).[12] Furthermore, these spheres can encapsulate molecules such as \(\text{1a}\) itself (Figure 1a)[12a,b] ferrocene (Figure 1b)[12c] \(\text{a}\)-carborane[12d,f] and also \(\text{C}_5\text{O}_6\).[12g] These reactions turned out to be very sensitive to many parameters such as stoichiometry, solvent, concentration and the used halide. Hence, also the nature of the \(\text{Cp}^\ast\) ligand in the pentaphosphaferrocene should profoundly affect.

![Figure 1](https://example.com/figure1.png)

Figure 1. Fullerene-like spheres based on 1a and \(\text{CuCl}\): a) 90-vertex supramolecule incorporating 1a; b) 80-vertex supramolecule incorporating \([\text{FeCp}^\ast]\).
the coordination behavior. Due to their rather straightforward synthesis in decalin as solvent (Scheme 1), a huge variety of pentaphosphaferrocenes is known so far with \( \text{Cp}^3 = \text{Cp}^5 \sim \eta^5-\text{C}_5\text{Me}_5\text{Et} \).\(^{[13]} \) \( \text{Cp}^3 = \eta^2-\text{C}_5\text{H}_5\text{Bu} \).\(^{[14]} \) \( \text{Cp}^4 = \eta^1-\text{C}_5\text{H}_5\text{Bu} \).\(^{[15]} \) \( \text{Cp}^5 = \eta^1-\text{C}_5\text{Me}_5\text{C}_5\text{H}_5\text{SMe} \).\(^{[14]} \) \( \text{Cp}^6 = \eta^1-\text{C}_5\text{Me}_5\text{C}_5\text{BuC}_5\text{H}_5 \).\(^{[17]} \)

In view of the large variety of \( \text{Cp}^5 \) -substituted pentaphosphaferrocenes, it is surprising that the parent compound \([\text{CpFe}(\eta^5-\text{P}_3)](1\text{~b})\) with an unsubstituted \( \text{Cp} \) ligand has never been reported. Especially this sandwich complex is of great interest as building block itself, as guest for the encapsulation in fullerene-like supramolecules and as general starting material in organometallic chemistry.

Although several detailed DFT computational studies predicted 1b to be stable,\(^{[18]} \) its synthesis remained an insuperable challenge. There is evidence that several attempts were in fact made to synthesize it. However, the use of decalin as solvent does not lead to the formation of 1b, but to a tetranuclear iron cluster (Scheme 2).\(^{[19]} \) Recently, we have shown that by using a higher-boiling solvent, \([\text{CpFe}(\eta^5-\text{P}_3)]\) as well as triple decker sandwich complexes can be obtained in much better yields than by earlier reported procedures and, by this means, for example, the hitherto unknown parent compound \([\text{Cp}^5\text{Mo}_2(\mu_3\eta^6-\text{S}_3\text{P}_3)]\) could also be synthesized for the first time.\(^{[20]} \)

Herein, we report on the first synthesis and the comprehensive characterization of the parent pentaphosphaferrocene \([\text{CpFe}(\eta^5-\text{P}_3)](1\text{~b})\). In order to compare its coordination behavior with that of the substituted pentaphosphaferrocenes, its reactivity towards \( \text{Cu} \) halides was studied. Among the obtained products is the first 3D polymer in the \( \text{cyclo-P}_3 \) ligand coordination chemistry. Furthermore, the ability of 1b was discovered to act as a template for the formation of unprecedented inorganic nano-sized spheres.

### Results and Discussion

#### Synthesis and characterization of 1b

For the synthesis of all hitherto synthesized pentaphosphaferrocenes a similar route was applied (Scheme 1). The thermolysis of \([\text{Cp}^5\text{Fe}(\text{CO})_3]_2\) with \( \text{P}_3 \) in decalin and subsequent chromatographic work-up afforded the desired complex as a green solid. When, however, this strategy is transferred to the \( \text{Cp} \) derivative the tetranuclear iron cluster \([\text{CpFe}(\eta^5-\text{P}_3)]\) is obtained exclusively (Scheme 2).\(^{[19]} \)

Since thermal conversion depends on the applied temperature, \([\text{CpFe}(\text{CO})_3]_2\) was allowed to react with \( \text{P}_3 \) in 1,3-disopropylnylbenzene with a higher boiling point in comparison to that of decalin (DIB, \( \text{bp} = 203 \text{ °C} \)), decalin: \( \text{bp} = 187–196 \text{ °C} \). Interestingly, this rather small temperature increase was most likely, the decisive factor to produce the unsubstituted parent compound 1b as sole product according to \( ^{31}\text{P}([\text{H}])\) NMR spectroscopy for the first time (Scheme 2). However, the aromatic character of the used solvent might also be crucial for the formation of 1b. The latter was purified by chromatographic workup to give a green powder in \( 8\% \) yield. To investigate whether the yield can be enhanced by a further increase of the temperature, the reaction was performed in 1,3,5-trisopropylbenzene (TIP, \( \text{bp} = 232–236 \text{ °C} \)). 1b can, in fact, be isolated after a significantly shorter reaction time of 2 hours, with the isolated yield remaining similar, due to the chromatographic workup.

Complex 1b is poorly soluble in aliphatic solvents such as \( \text{n-hexane} \), moderately soluble in toluene and \( \text{CH}_3\text{Cl}_2 \) and insoluble in \( \text{CH}_3\text{CN} \). As expected, the \( ^1\text{H} \) NMR spectrum of 1b shows one singlet at \( \delta = 3.39 \text{ ppm} \), which is upfield shifted compared to \([\text{FeCp}_3]\) (\( \delta = 4.04 \text{ ppm} \)).\(^{[21]} \) In the \( ^{31}\text{P}([\text{H}])\) NMR spectrum, one singlet appears at \( \delta = 169.5 \text{ ppm} \), thus revealing the equivalence of all the \( \text{P} \) atoms. This signal exhibits one of the farthest downfield shifts for the pentaphosphaferrocene compounds (signals range from \( \delta = 152.8 \text{ ppm} \) for \([\text{CpFe}(\eta^5-\text{P}_3)]\)\(^{[15]} \) to \( \delta = 173.6 \text{ ppm} \) for \([\text{Cp}^6\text{Fe}(\eta^5-\text{P}_3)]\)\(^{[15]} \), which therefore does not go hand in hand with the steric bulk, unlike previously assumed.\(^{[16,17]} \)

Furthermore, complex 1b sublimes at \( 80\text{ °C}/10^{-7} \text{ mbar} \), just as 1a did.\(^{[8]} \)

By layering a \( \text{CH}_3\text{Cl}_2 \) solution of 1b with \( \text{CH}_3\text{CN} \) in a thin Schlenk tube. 1b crystallizes as green prisms in the monoclinic space group \( \text{P2}_1//m \). Its molecular structure reveals a sandwich complex with \( \eta^1 \)-coordinated rings in a perfect eclipsed conformation, which is in accordance with all theoretical predictions (Figure 2).\(^{[18]} \) In contrast, due to the steric demand of the methyl substituents, the \( \text{Cp}^* \) derivative 1a deviates from the eclipsed conformation by \( 11.61^\circ \).\(^{[11b]} \) The interplanar angle of 1b is close to zero (0.56(8)°) and the angle \( \text{Cp}_\text{centered}-\text{Fe}-\text{P}_{\text{substrate}} \) of 179.87(4)° with both of them revealing a perfect sandwich complex almost free of distortion. The molecule 1b lies in a mirror plane (\( \text{C}_5 \) point symmetry) that bisects both \( \text{Cp} \) and \( \text{P}_3 \) rings (Figure 2) similarly to \( \text{Cp}_2\text{Ru} \)\(^{[22]} \) and \( \text{Cp}_3\text{Os} \)\(^{[23]} \) and the low-temperature orthorhombic modification of \( \text{Cp}_2\text{Fe} \).\(^{[24]} \)
contrast to ferrocene,\(^{24}\) \(1b\) demonstrates no phase transition in the temperature range of 123 K – 298 K. The diffraction experiment at room temperature of a single crystal of \(1b\) showed only increased thermal motion (see Supporting Information for details). A comparison of selected bond lengths of \(1b\) with optimized geometries based on DFT computations as well as with experimental data of \(1a\) is given in Table 1. It can be stated that all predicted values are in parts significantly longer than the experimentally observed ones. Furthermore, \(\pi\)-stacking interactions are present, since the \(1b\) molecules are arranged into head-to-tail chains (along the \(c\) axis) via \(\text{Cp–cyclo-P}_5\) interactions with interplanar distances of 3.71 Å or 3.78 Å at \(T = 123\) K or r.t., respectively (see Supporting Information for detail).

R. Winter et al. investigated the interesting redox behavior of the \(\text{Cp}^*\) derivative \([\text{Cp}^*\text{Fe(η}^1\text{-P}_5)](1a)\) and stated one-electron oxidation and reduction, which is reversible at high scan rates.\(^{25}\) However, the resulting complexes are not stable and readily dimerize to give \([1a]^{2+}\) and \([1a]^{2-}\), respectively. Their proposed structures were finally confirmed experimentally by our group.\(^{30}\) For a comparison, the electrochemical investigations were also performed for \(1b\) (Figure 3). Cyclic voltammetry data at a sweep rate of 0.1 V s\(^{-1}\) reveal an irreversible oxidation at a peak potential of \(-1.86\) (\(-2.05\) V for \(1a\)) as well as the corresponding anodic signal at \(-1.20\) V (\(-1.34\) V for \(1a\)) constitute a chemically reversible couple.

DFT computations of the electronic structure of \(1b\) show an orbital ordering that resembles that of \(1a\)\(^{27}\) (Figure 4). As compared with \(1a\), in \(1b\), the Highest Occupied Molecular Orbital (HOMO) as well as the Lowest Unoccupied Molecular Orbital (LUMO) lie slightly lower in energy than in \(1a\), rendering \(1b\) a weaker donor, but better acceptor (for the comparative energy level diagram of \(1a\) and \(1b\), see Supporting Information). The HOMO–LUMO gap in \(1b\) is 4.34 eV, whereas in \(1a\) it is 4.48 eV. The difference in the relative energy of the frontier orbitals in \(1a\) and \(1b\) is in line with the results of the CV measurements.

**Table 1.** Selected bond lengths and reported DFT optimized geometries of \(1b\) at 123 K (l.t.), \(1b\) at 298 K (r.t.) and \(1a\), respectively.

| Bond lengths [Å] | \(\text{Fe–Cp}^\text{p}(\text{centroid})\) | \(\text{Fe–P}_5(\text{centroid})\) | \(\text{P–P average}\) |
|------------------|-----------------------------|-----------------------------|-----------------------------|
| 1b               | 1.693(1)\(^{11}\)          | 1.536(1)\(^{11}\)           | 2.113(3)\(^{11}\)           |
| Padma Malar\(^{17b}\) | 1.706                       | 1.623                       | 2.148                       |
| Frenking et al.\(^{17c}\) | 1.716                      | 1.599                       | 2.163                       |
| Frison et al.\(^{17d}\) | 1.695                       | 1.578                       | 2.137                       |
| this work       | 1.712                       | 1.585                       | 2.127                       |
| 1a\(^{10b}\)    | 1.720(1)                    | 1.535(1)                    | 2.120(2)                    |
| 1b               | 1.698(1)\(^{11}\)          | 1.536(1)\(^{11}\)           | 2.10(1)\(^{11}\)            |
| Katsyuba et al.\(^{17e}\) | 1.706                      | 1.623                       | 2.148                       |

Figure 2. Molecular structure of \(1b\) in the crystal (side and top view).

Figure 3. Cyclic voltammogram of \(1b\) in \(\text{CH}_2\text{Cl}_2/\text{nBu}_4\text{NPF}_6\) solution at r.t. and \(\nu = 0.1\) V s\(^{-1}\).

Figure 4. Energy level diagram for \(1b\) calculated at the B3LYP/6-31+G(d,p) level of theory.

**Coordination behavior of \(1b\) towards Cu\(^{I}\) halides**

Due to the lone pairs on the \(P_5\) ring in combination with its outstanding five-fold symmetry, pentaphosphaferrrocenes represent excellent building blocks in supramolecular chemistry. Hence, the coordination behavior of \(1b\) towards Cu\(^{I}\) halides
was investigated (Scheme 3). A green solution of 1b in CH2Cl2 or toluene is layered with a colorless solution of CuX (X = Cl, Br, I) in CH2CN in a very thin Schlenk tube. The phase boundary turns yellow-orange and small crystals of [(Cp*Fe)5,1,1,1,1,1-(P3)2]Cu2X2(μ-X)4 (2a: X = Cl, 2b: X = Br, [(CpFe(n5,1,1,1,1,1-P5)5)CuCl]n (3) and [(CpFe(n5,1,1,1,1,1-P5)5)3]Cu(μ-I))n (4), respectively, start to grow after a few hours already. Due to the same (in)solvability, the CuI-containing polymers 3 and 4 cannot be separated. Unfortunately, regardless of several attempts, a selective synthesis is not feasible either, since they contain the same molar ratio of 1b and CuI. Based on the different colors, orange for 3 and red for 4, only a manual separation by crystal picking separates the products.

Compounds 2a and 2b are isomeric and crystallize as very thin orange plates in the triclinic space group P1. Single-crystal X-ray structure analysis reveals 2D polymers with a 1,2,3,4-coordination mode of the cyclo-P3 ligand (Figure 5a). The coordination of four P atoms of the ring occurred before in three previous examples, namely [(Cp4Fe(n5-P5))2(Cul)]n, (Cp8 = Cp*, Cp3 = Cp3)[11c,28] and [(CpFe(n5,1-P5))2(Cu(GaCl3))2]n.[11b] However, 2a and 2b differ from these examples in their connectivity and show an unprecedented structural motif. In addition to (Cu,P3) hexagons and (Cu,X)2 squares, also seven-membered (Cu,P3) rings are present. This linking pattern forms a planar 2D sheet structure with an orientation of the (CpFe) units alternating upwards and downwards. Note that they now deviate from the eclipsed conformation of the Cp ligand to the cyclo-P3 unit by ≈14°. Interestingly, 2a,b represent a novel layer topology for pentaphosphaferrocenes with 3-coordinated Cu+ and 4-coordinated Cu+ units serving as nodes and halide spacers (see Supporting Information).[29]

Compound 3 crystallizes in the monoclinic space group P21/c. Its 2D polymeric network consists of connected rectangles of 1b and four-membered CuJ3 rings (Figure 5b). Two of the four (Fe-Cp) units per rectangle are orientated towards each other. The cyclo-P3 moieties show a 1,3-coordination mode, which had been unknown for pentaphosphaferrocenes in coordination polymers for a long time. Some years ago, we were able to obtain two examples, [[Cp*Fe(n5-P5)2](Cu)]n[11c] and [[Cp4Fe(n5,1-P5)2]Ag]n[[Al(OC(CF3)3)]n.[11d] both, however, forming infinite chain 1D polymers. The only example of a supramolecule based on a 1,3-coordination mode of [Cp(Fe)n-1-P2] with—interestingly—a minimum amount of metal cations—has been obtained only very recently.[30] In contrast, 3 forms two-dimensional layers. When the bridging iodine atoms and the 1,3-coordinated 1b molecules are treated as spacers and the Cu atoms as nodes of the polymeric structure, the honeycomb hcb topology of the layer becomes evident.[29,31]

Compound 4 crystallizes as red prisms in the orthorhombic space group Pna21. Remarkably, it is a constitutional isomer of 3, having the same sum formula [[CpFe(n5-P5)]Cu(μ-l)], but different connectivity, representing the first example of a 3D pentaphosphaferrocene-based polymer. This is astonishing, since all obtained pentaphosphaferrocene-based polymers are either 1D or 2D.[11] In 4, two P atoms per P3 ring are connected to Cu, resulting in a 1,3-coordination mode as it is observed in 3 (Figure 6). As in 3, Cu possesses the tetrahedral environment with the bridging coordination of iodide. In contrast to 3, no CuJ3 rings but infinite (CuI) zigzag chains are formed in 4 (Figure 6). Its net topology can be assigned to the dia type,[26,32] which is for example, known for diamond (Figure 7).

Among these polymers, π-stacking interactions, similar to the ones found in 1b, do not occur. Despite rather short inter-
layer distances of 3.22 Å in 2a and 3.27 Å in 2b, the layers are mutually shifted and do not afford a direct contact of the π-systems. In both 3 and 4, the π-systems are not parallel, and all contacts involving P atoms are within the range of van der Waals interactions.

All four coordination polymers are insoluble in common solvents such as hexane, toluene, CHCl₃, CH₂CN, Et₂O and thf. They can only be dissolved in pyridine, albeit accompanied by complete fragmentation. Hence in the ¹H and ³¹P¹H NMR spectra, respectively, only the singlet for 1b can be detected.

Inclusion of 1b in fullerene-like spheres

Compound 1b does not only represent an interesting building unit, but is also excellently suited for the encapsulation into pentaphosphaferrocene-based supramolecules. Recently, we were able to show that ferrocene [Fe(P₄)] can be incorporated in an 80-vertex sphere consisting of 12 molecules of 1a and 20 CuCl units.[12a,b] The scaffold only consists of five- (P₅) and 20 six-membered (Cu₆P₄) rings and shows I₃-Cₙ₀ fullerene topology. Also, pentaphosphaferrocene 1a itself acts as a template and is enclosed by a 90-vertex supramolecule.[12a,b] This sphere exhibits a slightly larger scaffold diameter due to the larger size of 1a. More tellingly, one can imagine the 80-vertex ball as being divided into two equal half shells with a [(Cu(CH₂CN))₃]X₂ (X = Cl, Br) belt combining them. Since the size of 1b is between, the question arises as to which host will be the preferred one.

To answer this question, a dark green solution of 1a and 1b in CH₂Cl₂ (molar ratio 1a:1b = 9:1) is layered with a colorless solution of CuX (X = Cl, Br, I), respectively. Remarkably, in all three reactions, black rhombohedra of [CpFe(η⁵-P₅)]@[CpFe(η⁵-P₅)](CuX)₃ (5a: X = Cl, n = 2.4; 5b: X = Br, n = 2.4; 5c: X = I, n = 0.95) are formed immediately.[13b] All three compounds are isosctrical and crystalline in the trigonal space group R₃. In their structures, one molecule of 1b is incorporated into the smaller 80-vertex nanoball regardless of which halide is used (Figure 8), showing the distinctly preferred encapsulation of the pentaphosphaferrocene guest 1b. Note that 5c displays the first fullerene-analogue containing copper iodide. Most previous attempts starting with Cp and 1a resulted in the formation of polymeric products. Merely few P₄-based supramolecules with Cp are known, without any of them, however, following the fullerene topology.[12b,h,12c,h,12d,h,28] Therefore, the selective formation of 5c is very remarkable and reveals the perfect template properties of 1b.

The host molecules in 5a-c consist of 12 moieties of 1a, which show an all-P coordination mode to copper. The complete 80-vertex scaffold would contain 20 CuX (X = Cl, Br, I) units forming 30 (Cu₆P₄) six-membered rings. However, in all three spherical compounds, the scaffold exhibits some number of CuX vacancies. This phenomenon was also observed for a similar system with o-carborane and ferrocene as guests.[12a,h] As a consequence, the ideal number of 20 in the Cu₆P₄ scaffold is reduced per supramolecule to 15.9 for 5a, 17.4 for 5b and 16.4 for 5c (Figure 8b) giving rise to non-stoichiometric solid solutions of metal-deficient supramolecules. Some solvent CH₂Cl₂ molecules point into the vacant holes in the copper-phosphorus scaffold that can cause a partial ordering of supramolecules, similar to toluene molecules.[12a] Another consequence of these ‘holes’ for the adjacent cyclo-P₄ ligands is the stochastic reduction of the pentacoordination, in most cases to a tetra- or three-coordination to copper.

The outer diameter of all three supramolecules is 2.12 nm and does not depend on the nature of the halide, since the Cp* ligands protrude further. The inner diameters are determined by the distance between opposite cyclo-P₄ ligands and are therefore identical with a value of 0.77 nm. These dimensions are in good agreement with previously obtained 80-vertex spheres.[12a,c,h] Furthermore, the spherical cavity shows the appropriate size for one molecule of 1b (0.70×0.67 nm).

The guest molecule is present in each cavity of the supramolecules 5a-c as proved by the occupancy factors of the Fe atoms in the center. All other atoms are severely disordered over twelve positions even at 10 K (5a), partly related by symmetry (see Supporting Information for details). In contrast to a ferrocene encapsulation where the distinctive face-to-face orientation of Cp ligands towards the cyclo-P₄ ligands of the host points out possible Cp–P₄ π-stacking host–guest interactions,[12h] the cyclo-P₄ ligands of the 1b guest do not demonstrate any preferable orientation with respect to the host supramolecule. Angles between the P₄ aromatic systems belonging to 1b and the host molecules 5a-c vary in a range between 0.8(3)° and 23.5(9)° with the corresponding P–P contacts being beyond the sum of van-der-Waals radii of 3.6 Å (see Supporting Information for details).[34]

The supramolecules 5a-c are all obtained by diffusion reactions and their synthesis can always be accompanied by the formation of polymeric networks [Cp*Fe(η⁵-P₅)]@[CuX]₃ (11a,b) (X = Cl, Br, I). In addition, for X = Cl, Br, also the 90-vertex spheres [Cp*Fe(η⁵-P₅)]@[CuX]₃(C₉H₈CN)₃ (11c,d) can be formed within these self-assembly processes. However, a precise monitoring during the diffusion process revealed that, for X = Cl, Br, black rhombohedral of 5a/5b crystallize at the phase boundary first. After approximately one to two days, brownish

![Figure 8](image-url)
plates of \([\text{Cp}^*\text{Fe}(\eta^5-P_3)(\text{CuX})]_n\) are visible at the bottom of the Schlenk tube. Finally, after complete diffusion, rods of the crystalline phase containing 90-vertex supramolecules start to appear. Therefore, to obtain pure 5a, one has to collect the crystals as soon as possible only from the Schlenk wall with a spatula (see Supporting Information). That way, pure 5a is obtained in still very good crystalline yields of 64%. Unfortunately, this separation procedure is not possible for \(X=I\), since crystals of 5c and \([\text{Cp}^*\text{Fe}(\eta^5-P_3)(\text{Cul})]_n\) start to grow in the same areas concomitantly at random.

All obtained supramolecules are completely insoluble in common solvents such as hexane, toluene, \(\text{CH}_2\text{CN}, \text{Et}_2\text{O}\) and thf, but can be dissolved in pyridine at the cost of fragmentation. Therefore, in the corresponding \(^1\text{H}\) and \(^31\text{P}[^1\text{H}]\) NMR spectra, only signals of the starting complexes 1a and 1b are observed, additionally proving the encapsulation of 1b. On the other hand, this also means that the encapsulated pentaphosphaferrocene 1b can be released by disassembling of its host.

Surprisingly and contrary to previously reported 80-vertex supramolecules, which are completely insoluble in any organic solvent,\(^{12,26,29}\) 5a and 5b are slightly soluble in \(\text{CH}_2\text{Cl}_2\) (but still very poorly). Thus, a characterization by NMR spectroscopy is enabled. In the \(^31\text{P}[^1\text{H}]\) NMR spectrum of 5a, three very broad signals at \(\delta=70, 76\) and 103 ppm, one sharp singlet at \(\delta=152.1\) ppm and one slightly broadened singlet at \(\delta=170.5\) ppm can be observed. According to a detailed NMR study of soluble supramolecules with \(\text{Cp}^{\text{Bn}}\)-based pentaphosphaferrocene, the broad signals can be assigned to the coordinated P atoms of spheres with varying metal-deficiency\(^{138}\). In addition, a small amount of 1a might be released, causing the singlet at \(\delta=152.1\) ppm. Due to the broadening, the singlet at \(\delta=170.5\) ppm is assigned to the encapsulated complex 1b, thus being slightly downfield-shifted compared to free 1b (in \(\text{CD}_2\text{Cl}_2\): \(\delta=168.6\) ppm). This observation is in contrast to previously reported guest molecules, which all show a slight shift to higher field. Therefore, 1b displays the first template which might rather act as an electron donor. The quality of the \(^31\text{P}[^1\text{H}]\) NMR spectrum of the analogous compound 5b is already quite poor, since its solubility is even worse. Nevertheless, also two singlets for 1a and 1b as well as one very broad signal for 5b can be observed. Other broad signals, as they were observed for 5a, can only be adumbrated and disappear below the noise floor.

Conclusions

In summary, the first synthesis and comprehensive characterization of the parent pentaphosphaferrocene \([\text{Cp}^*\text{Fe}(\eta^5-P_3)]\) (1b) are presented. The replacement of decalin by the even higher-boiling solvents DIB or TIP makes the general route feasible for the formation of the so far missing example of a parent complex. The X-ray structure analysis reveals an eclipsed sandwich complex with slightly shorter bond lengths than the theoretically predicted ones. The DFT computations also reveal a slightly stronger acceptor and weaker donor ability, compared to the \(\text{Cp}^*\) derivative 1a. The cyclic voltammetry data show an irreversible oxidation and a reversible reduction. To investigate the coordination behavior of 1b, it was reacted with CuX (X = Cl, Br, I). In all reactions, the formation of unprecedented 2D polymers (2a, 2b and 3) and even the first 3D polymer (4) based on pentaphosphaferrocene is observed. The networks 2a and 2b show a 1,2,3,4-coordination mode of the cyclo-P3 ligand, whereas, in 3 and 4, a 1,3-coordination is present. At the same time, no sign of the formation of 1b-based supramolecules was observed. Furthermore, the incorporation of 1b as a guest into 80-vertex nanoballs (5a–c) was examined. The host molecules differ in the halide and, for the first time, an iodine-containing supramolecule with fullerene topology is obtained. Its behavior in solution shows that 1b remains incorporated in the host in \(\text{CH}_2\text{Cl}_2\), whereas fragmentation and therefore the release of the template are observed in donor solvents such as pyridine. Moreover, 1b displays the first template for fullerene topological spheres, showing to act as an electron donor to the overall host assembly. All in all, the influence of the unsubstituted parent Cp ligand is demonstrated: starting from different conditions during its synthesis through its deviating coordination behavior towards copper(I) to changes in its host-guest chemistry owing to its smaller size. Moreover, the successful synthesis of 1b opens the possibility to explore the preference of organometallic transformations occurring either on the Cp or the cyclo-P3 ligand, a fascinating comparison for future work.

Experimental Section

Crystallographic data: Deposition numbers 2054500 (1b), 2054499 (1b r.t.), 2049560 (2a), 2049561 (2b), 2049562 (3), 2049563 (4), 2054501 (5a), 2054504 (5a 10K), 2054503 (5b), 2054502 (5c) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of interest

The authors declare no conflict of interest.

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