

Giant Rugby Ball $[\{\text{Cp}^{\text{Bn}}\text{Fe}(\eta^5\text{-P}_5)\}_{24}\text{Cu}_96\text{Br}_{96}]$ Derived from Pentaphosphaferrocene and CuBr_2

Claudia Heindl,[†] Eugenia V. Peresyphkina,^{‡,§} Alexander V. Virovets,^{‡,§} Werner Kremer,[#] and Manfred Scheer^{*,†}

[†]Institute of Inorganic Chemistry, University of Regensburg, 93040 Regensburg, Germany

[‡]Nikolaev Institute of Inorganic Chemistry, Siberian Division of RAS Acad., Lavrentyev str. 3, 630090 Novosibirsk, Russia

[§]Novosibirsk State University, Pirogova str. 2, 630090 Novosibirsk, Russia

[#]Institute of Biophysics and Physical Biochemistry, University of Regensburg, 93040 Regensburg, Germany

Supporting Information

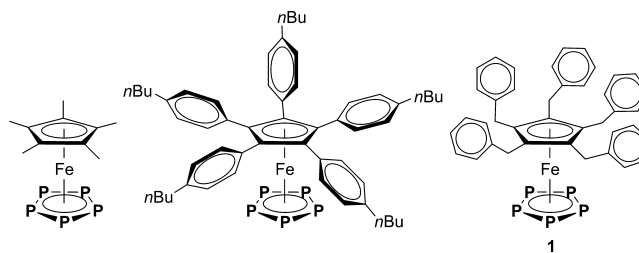
ABSTRACT: The self-assembly of $[\text{Cp}^{\text{Bn}}\text{Fe}(\eta^5\text{-P}_5)]$ ($\text{Cp}^{\text{Bn}} = \eta^5\text{-C}_5(\text{CH}_2\text{Ph})_5$) with CuBr_2 leads to the formation of an unprecedented rugby ball-shaped supramolecule consisting of 24 units of the pentaphosphaferrocene and an extended CuBr framework, which does not follow the fullerene topology. The resulting scaffold of 312 noncarbon atoms reveals three different coordination modes of the cyclo-P_5 ligand including a novel π -coordination. The outer dimensions of 3.7×4.6 nm of the sphere approach the range of the size of proteins. With a value of 32.1 nm^3 , it is 62 times larger in volume than a C_{60} molecule. Surprisingly, this giant rugby ball is also slightly soluble in CH_2Cl_2 .

The construction of discrete nanosized clusters and supramolecules is a fascinating frontier in modern molecular chemistry. A challenge within this field is the constant increase of the size to enter the field of nano and material science. For the design of ever-larger spheres two different approaches of connectivity are applied. In inorganic chemistry, the clusters are held together mostly by covalent bonds, as it is the case for fullerenes,¹ highly symmetric polyoxometallates,² coinage chalcogenide clusters,³ or (inter)metalloid clusters.⁴ Among them are the largest structurally characterized aggregates: concerning the size, the “hedgehog” cluster $[\text{H}_x\text{Mo}_{368}\text{O}_{1032}(\text{H}_2\text{O})_{240}(\text{SO}_4)_{48}]^{48-}$ ($x \approx 16$) reaches an outer diameter of ca. 6 nm.⁵ Regarding the largest number of metal atoms: the cluster $[\text{Ag}_{490}\text{S}_{188}\{\text{S}(t\text{-C}_5\text{H}_{11})_{114}\}]$ of Fenske et al. contains 490 metal atoms.⁶ The other approach, based on supramolecular coordination chemistry,⁷ utilizes weaker interactions such as hydrogen bonds, π - π interactions and coordinative bonds and involves metal salts or complexes and multitopic organic linkers. Thereby, the design of a large variety of spheres, though of smaller size, is enabled, and these supramolecules can often act as hosts for small guest molecules.⁸

We are interested in the expansion of this self-assembly approach to organometallic connecting units and use $[\text{Cp}^{\text{R}}\text{Fe}(\eta^5\text{-P}_5)]$ ($\text{Cp}^{\text{R}}: \text{Cp}^{\text{Bn}} = \eta^5\text{-C}_5(\text{CH}_2\text{Ph})_5$ (**1**); $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{Cp}^{\text{Et}} = \eta^5\text{-C}_5\text{Me}_4\text{Et}$; $\text{Cp}^{\text{BIG}} = \eta^5\text{-C}_5(4\text{-}n\text{BuC}_6\text{H}_4)_5$) as building blocks for this purpose (**Chart 1**). These pentaphosphaferrocene

complexes provide the advantage of phosphorus as donating atoms and a 5-fold symmetry provided by the cyclo-P_5 ring.⁹

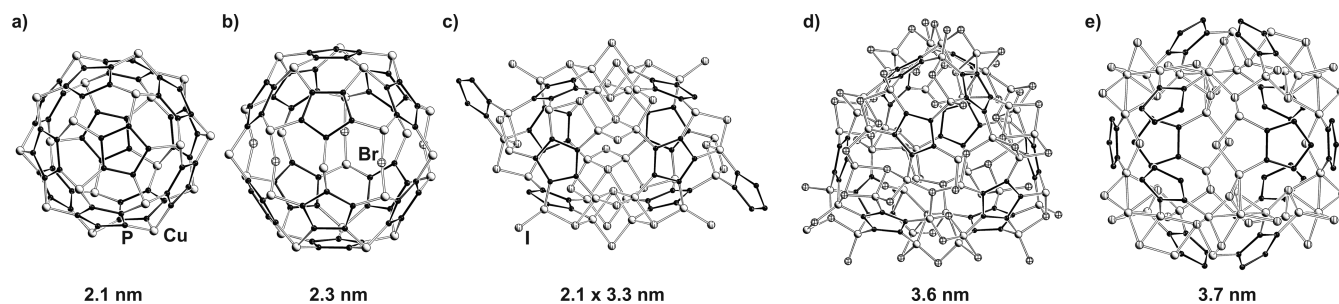
Chart 1. Phosphaferrocenes $[\text{Cp}^{\text{R}}\text{Fe}(\eta^5\text{-P}_5)]$ ($\text{Cp}^{\text{R}} = \text{Cp}^*, \text{Cp}^{\text{BIG}}, \text{Cp}^{\text{Bn}}$) for the Construction of Discrete Supramolecules



In combination with Cu(I) halides these benefits gratifyingly lead to the formation of nanosized supramolecules with and beyond the fullerene-like topology. Depending on the substitution pattern of the Cp^{R} ligand, various spheres with different scaffolds, shapes, and outer diameters have been obtained.¹⁰ A selection of the obtained scaffolds is shown in **Chart 2**. For example, **Chart 2a** shows a sphere that follows the isolated pentagon rule (IPR)^{10b,e} and has fullerene topology displaying a carbon-free $I_h\text{-C}_{80}$ analogue. The incorporation of a middle belt leads to a slightly larger ball (**Chart 2b**) with 90 noncarbon vertices.^{10e,h} Even larger supramolecules with deviating topologies and extended CuX ($\text{X} = \text{Br}, \text{I}$) frameworks can also be obtained (**Chart 2c–e**).^{10c,d,g} Among them, there is one common feature concerning the number of pentaphosphaferrocene units per supramolecule: it is always equal to 12 like for fullerene-related balls^{10a,b,e,h} (**Chart 2a,b**) and less than^{10d,f} or equal to^{10c} 12 for spheres with deviating topologies (**Chart 2c–e**). A slightly higher number of cyclo-P_5 moieties, namely 13, occurred solely once, when C_{60} is encapsulated into a 99-vertex sphere.^{10g} The hitherto largest spheres are constructed by sterically demanding phosphaferrocenes, such as the Cp^{Bn} and Cp^{BIG} derivative. The record size of 3.7 nm is held by $[\{\text{Cp}^{\text{Bn}}\text{Fe}(\eta^5\text{-P}_5)\}_{12}(\text{CuI})_{54}]$, owing to the presence of an extensive CuI aggregate (**Chart 2d**).^{10c}

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Chart 2. Inorganic Scaffolds of Selected Pentaphosphaferrocene-Based Supramolecules^a

^a(a) 80-vertex ball, $\text{Cp}^{\text{R}} = \text{Cp}^{\text{*}}$, Cp^{Bn} ;^{10b,e} (b) 90-vertex ball, $\text{Cp}^{\text{R}} = \text{Cp}^{\text{*}}$;^{10e,h} (c) cuboid-shaped sphere, $\text{Cp}^{\text{R}} = \text{Cp}^{\text{*}}$;^{10d} (d) tetrahedral shaped supramolecule, $\text{Cp}^{\text{R}} = \text{Cp}^{\text{Bn}}$;^{10b} (e) 168-vertex ball, $\text{Cp}^{\text{R}} = \text{Cp}^{\text{Bn}10c}$.

Herein we report on the synthesis and characterization of the unprecedented giant rugby ball $[\{\text{Cp}^{\text{Bn}}\text{Fe}(\eta^5\text{-P}_5)\}_{24}\text{Cu}_{96}\text{Br}_{96}] \cdot 6.2\text{CH}_2\text{Cl}_2 \cdot 4.6\text{C}_7\text{H}_8 \cdot 2.4\text{CH}_3\text{CN}$ (**1**) obtained by the reaction of **I** with CuBr_2 .

Neither such a high number of P_5 units nor such an extended CuBr framework has been found in a supramolecule yet (Figure 1). The outer size of 4.6×3.7 nm is larger than all the other examples based on 5-fold symmetric building blocks.

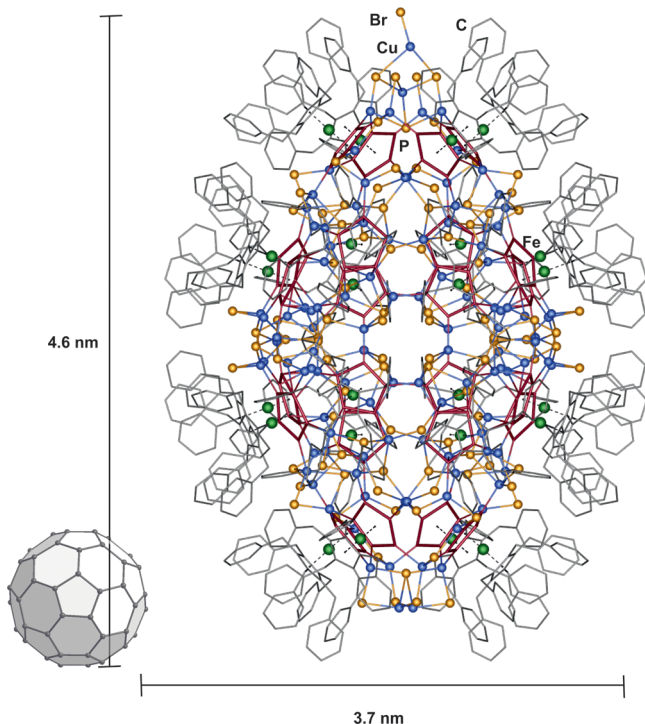


Figure 1. Molecular structure of **1**. Hydrogens, solvents and minor parts of disorder are omitted for clarity. C_{60} is depicted for comparison.

When a dark green solution of CuBr_2 in CH_3CN is added to a green solution of **I** in CH_2Cl_2 , an immediate color change to intense red is observed. After 1 day of stirring and removal of the solvent, the residue is dissolved in CH_2Cl_2 and carefully layered with toluene. Within a few weeks, red rods of **1** crystallize, mostly accompanied by the crystallization of black blocks of the 80-vertex supramolecule $[(\text{I})_{12}(\text{CuBr})_{20-x}]$ ($x < 7$) (**II**; Chart 2a). The latter molecule was obtained by a different route before and its formation and behavior in solution was comprehensively studied.^{10b} Investigations on a selective synthesis reveal that the

amount of acetonitrile seems to play a crucial role in the formation of **1** (for details see SI). Therefore, the yields of **1** vary, though with an astonishing maximum of 84% of pure **1**.

Compound **1** crystallizes in the chiral orthorhombic space group $I222$ with unit cell dimensions of $a = 33.2127(2)$ Å, $b = 42.4597(2)$ Å, and $c = 50.9189(3)$ Å. X-ray structural analysis reveals that the giant sphere is built by 24 units of **I** connected by 96 units of CuBr (Figure 1). In the crystal the supramolecules form a distorted face-centered cubic packing (for figures, see SI).

In **1**, the *cyclo*- P_5 ligands reveal three different coordination modes to copper (Figure 2): **A**, each phosphorus atom shows a

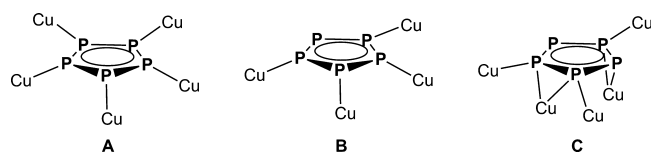


Figure 2. Illustration of the different coordination modes of the P_5 ligand in **1**.

η^1 -coordination to Cu ($10 \times \{\text{Cp}^{\text{Bn}}\text{Fe}(\eta^{5:1:1:1:1}\text{-P}_5)\}$); **B**, four P atoms feature a η^1 -coordination ($6 \times \{\text{Cp}^{\text{Bn}}\text{Fe}(\eta^{5:1:1:1:1}\text{-P}_5)\}$); and **C**, in addition to a η^1 -coordination of three P atoms, two P–P edges surprisingly each show a η^2 -bond to copper ($8 \times \{\text{Cp}^{\text{Bn}}\text{Fe}(\eta^{5:2:2:1:1:1}\text{-P}_5)\}$). Both σ -coordination modes are well-known for this ligand since **A** is present in all spherical supramolecules¹⁰ and **B** is obtained in two polymeric products.^{10c,11} In contrast, type **C** is unprecedented for this ligand. Comparative studies of $[\text{Cp}^{\text{*}}\text{Fe}(\eta^5\text{-E}_5)]$ ($\text{E} = \text{P}, \text{As}$) rather revealed that the σ -interaction is clearly preferred by the phosphorus derivative, whereas it is the π -coordination mode for the arsenic analogue.¹² There are few exceptions with only one η^2 -bond per P_5 ligand,^{10a,b,11} though **1** displays the first compound with two η^2 -bonds per P_5 ring.

In **1**, the different coordination modes show a noticeable effect on the corresponding bond lengths. The σ -Cu–P distances range between 2.210 and 2.293 Å and are therefore significantly shorter than the π -Cu–P bonds (2.345–2.420 Å). Furthermore, also the P–P bond lengths in the still planar *cyclo*- P_5 rings are affected: Those, which are involved in the π -bonding, range from 2.116 to 2.133 Å and are therefore slightly elongated in comparison to the free complex **I** (2.110(1) Å).¹³ On the contrary, the P–P bond lengths in types **A** and **B** are quite uniform (2.066–2.113 Å) and slightly shorter than in **I**. The Cu atoms in **1** show a characteristic tetrahedral environment, whereas the bromine atoms act as terminal as well as bridging (μ_2, μ_3, μ_4) ligands. The constructed framework includes a variety of different ring sizes, such as

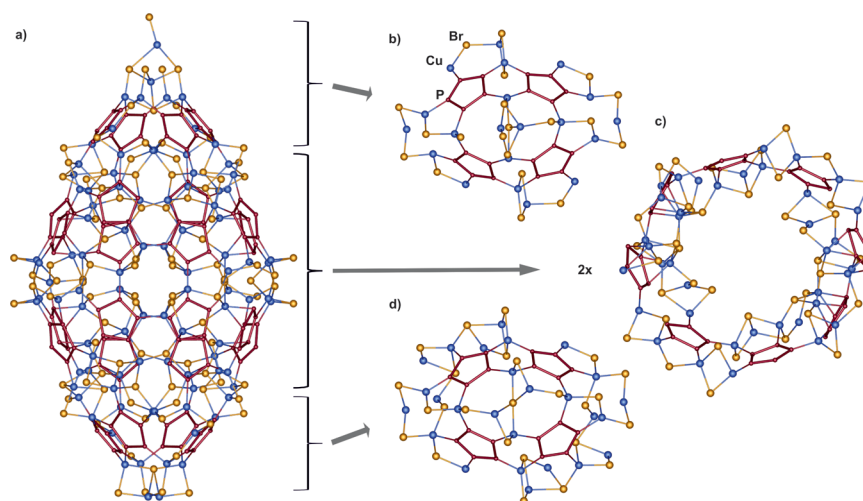


Figure 3. (a) Inorganic scaffold of **1** containing 312 atoms; top view of the (b) upper part, (c) middle part, and (d) lower part.

{Cu₂Br₂}, {P₂Cu₂Br}, {P₂Cu₃Br}, {P₄Cu₂}, {Cu₃Br₃}, and {P₂Cu₄Br₃} rings, hence a comparison to the fullerene topology would be too far-fetched.

The whole sphere of **1** can formally be divided into two caps, which frame two identical middle belts (Figure 3). The caps each comprise four pentaphosphaferrocene molecules bound to Cu atoms in a 1,2,3,4,5-mode (type A). In addition, the ends show a severe disorder of Cu and Br positions, respectively (cf. SI). Therefore, two different noncontradictory possibilities are shown as the upper and lower parts in Figure 3b and Figure 3d, respectively. However, each middle belt contains eight moieties of **1** with all three observed coordination modes (1 × A, 4 × B, 3 × C; cf. Figure 2).

In total, the scaffold of **1** consists of 312 atoms (120 P, 96 Cu, 96 Br; Figure 3a; for a stereogram, see SI). This number far exceeds all hitherto reported pentaphosphaferrocene-based spheres, which mostly contain 80 up to 100 framework atoms. Recently we have shown that the use of **1** instead of the well explored Cp* derivative [Cp*Fe(η⁵-P₅)] allows the agglomeration of more CuX units (X = Br, I); however, the maximum numbers of scaffold atoms amount to 162 for X = Br (Chart 2d)^{10b} and 168 for X = I (Chart 2e),^{10c} if the reaction conditions regarding the amount of acetonitrile are different from those of the reaction yielding **1** (see above). The use of the even more sterically demanding Cp^{BiG} derivative allows the isolation of a 170-vertex skeleton.^{10a} Therefore, in **1**, almost twice the number is present.

Concerning the size, the giant rugby ball **1** reaches 4.6 nm in length and 3.7 nm in width (Figure 1).¹⁴ These values again exceed all other [Cp^RFe(η⁵-P₅)]-containing supramolecules (cf. Chart 2a–d). Though **1** has fewer metal atoms than [Ag₄₉₀S₁₈₈(StC₅H₁₁)₁₁₄],⁶ it is larger than this hourglass shaped cluster (2.8 × 3.1 nm). Remarkably, this size is already on the verge of protein dimensions, e.g., hemoglobin shows a diameter of 5 nm.¹⁵

For another spectacular comparison: the diameter of the Buckminster fullerene C₆₀ is close to 1 nm; therefore, compound **1** is almost five times as long and four times as wide (Figure 1).¹⁶ Since the shape of **1** is similar to that of a protrude ellipsoid, the volume of the supramolecule can be calculated and amounts to 32.1 nm³ with the values of the half axes being 2.3, 1.85, and 1.8 nm, respectively.¹⁴ Hence staggeringly, the volume of **1** is 62 times larger than the ball-shaped C₆₀ fullerene (V = 0.52 nm³).

Despite the copper halide framework, which is partly extended into the inside, the size of the inner cavity still amounts to 2.5 × 1.2 nm.¹⁴ It is filled with disordered CH₂Cl₂ and CH₃CN molecules.

Note that in the rugby-ball **1** as well as in the 80-vertex ball **II** only Cu(I) units are present, though starting from CuBr₂ and thus indicating a reduction. This is also supported by the absence of a signal in the EPR spectrum of **1** in CH₂Cl₂ at ambient temperatures as well as at 77 K. However, no corresponding oxidation product could be identified. This phenomenon has already been observed, when [Cp*Fe(η⁵-P₅)] or [{CpMo(CO)₂}]₂(η²-P₂) is combined with Cu(II) halides.^{11,17} Recently, our group succeeded in the isolation of the oxidation product of [Cp*Fe(η⁵-P₅)], which is a dimer of the formula [Cp*Fe(η⁴-P₅)]₂²⁺ and readily decomposes in solutions of donor solvents.¹⁸ Therefore, an analogous reaction might also take place during the formation of **1** and **II**.

Compound **1** is insoluble in common solvents like hexane, toluene, and Et₂O. However, due to the benzyl substituents, **1** is slightly soluble in CH₂Cl₂, which is absolutely remarkable for these giant aggregates. In the ¹H NMR spectrum of crystals of **1** in CD₂Cl₂, broad multiplets for the methylene groups (δ = 3.6–4.9 ppm) as well as for the aromatic protons (δ = 5.8–7.0 ppm) with the correct integral ratio of 2:5 are detected (see SI). Yet, in the ³¹P{¹H} NMR spectrum no signal is observed, even when applying more than 10,000 scans or recording it at low temperature (T = 193 K). Nonetheless, signals for both nuclei corresponding to free molecules of **1** are not visible, which should appear already at low concentrations due to their sharpness. This indicates the persisting coordination of Cu (nuclear spin I = 3/2) to the cyclo-P₅ ligand in solution. In the ³¹P{¹H} solid state NMR spectrum of **1**, a broad multiplet at δ = 155 ppm (ω_{1/2} = 2460 Hz) is detected (for spectrum see SI), which is comparable to ³¹P{¹H} MAS studies of other pentaphosphaferrocene containing assemblies with more than three coordinating phosphorus atoms.^{10e,11,19} Due to similar chemical shifts, a distinction of the different coordination modes is impossible. In addition, the cationic ESI mass spectrum shows small peaks corresponding to the fragments [(I)₂Cu₃Br₂]⁺, [(I)₂Cu₂Br]⁺, and [(I)₂Cu]⁺ at m/z = 1803.2, 1659.5, and 1515.4, respectively. However, in the anionic ESI-MS spectrum, only peaks assignable to copper bromide units up to [Cu₃Br₄]⁻ are obtained.

In summary, the rugby ball-shaped sphere **1** is obtained by the self-assembly of the pentaphosphaferrocene **1** with CuBr₂. Whereas for spherical molecules the number of P₅ rings was hitherto restricted to a maximum of 13, with 24 moieties of **1** in compound **1**, this trend is no longer true. Including the exceptional extended Cu₉₆Br₉₆ framework, the inorganic scaffold consists of 312 atoms. The outer size of the entire sphere amounts to 3.7 nm in width and 4.6 nm in length with a corresponding volume of 32.1 nm³; hence, it is one of the largest discrete supramolecules, which has been yet structurally characterized. More vividly, it is even 62 times larger in volume than the C₆₀ fullerene ($V = 0.5 \text{ nm}^3$). The *cyclo*-P₅ ligands in **1** show three different coordination modes, for which one of them includes the unprecedented η^2 - π -coordination to copper. In addition, the giant molecule is slightly soluble in CH₂Cl₂, which allowed NMR spectroscopic investigations. Since **1** provides a cavity, future investigations will be concerned with the replacement of the enclosed solvent molecules and potential incorporation reactions.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06835.

Experimental section, crystallographic details, and spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*manfred.scheer@ur.de

Notes

The authors declare no competing financial interest.

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