DOI: 10.1002/anie.201005910

Organometallic Nanocapsules

An Organometallic Nanosized Capsule Consisting of *cyclo*-P_5 Units and Copper(I) Ions**

*Stefan Welsch, Christian Gröger, Marek Sierka, and Manfred Scheer**

Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 70th birthday

The assembly of molecular capsules is a fascinating and ongoing topic in current chemistry. Depending on their size and composition, molecular capsules can serve as reaction vessels and supramolecular containers for specific guest molecules.[1] The majority of reported systems are built from organic oligotopic moieties (N, O, and S linkers) that are connected by complementary interactions based on hydrogen bonding or coordination to Lewis acidic metals.[2] Sometimes π-stacking and CH⋯π interactions between host and guest molecules play an important role for such organic building blocks.[3] For inorganic systems, capsulelike metal–ligand aggregates are known, in which polyoxometalates of transition metals,[4] and, more recently, main-group-metal moieties such as tin sulfides[5] have been connected by organic linker molecules. Completely inorganic capsules have been described only for polyoxometalates. These covalently bound systems can act as molecular containers with flexible porous surfaces.[4d,6] In contrast, no organometallic capsules with weak noncovalent interactions between the cavitands have been reported to date. Recently, we demonstrated the potential of organometallic polyphosphorus donor ligand complexes for the self-assembly of spherical fullerene-like supramolecules. Here, the *cyclo*-P_5 ligand complex [Cp*Fe(η^5-P_5)] (**1**; Cp* = η^5-C_5Me_5)[7] and the *cyclo*-P_4 ligand complex [Cp″Ta(CO_2)(η^4-P_4)] (Cp″ = η^5-$C_5H_3tBu_2$-1,3) were used as linking units between copper(I) halides.[8,9] The thermodynamically favored formation of polymers[8] is strongly dependent on the reaction conditions, and can be avoided so that only spherical supramolecules are obtained.[9] In all of these compounds, the *cyclo*-P_5 ligand of [Cp*Fe(η^5-P_5)] serves as a fivefold symmetric building block that leads to structural motifs similar to those of the fullerenes. In contrast, we have now found that by variation of solvents and, more importantly, the stoichiometry, a novel threefold symmetric aggregation occurs that results in the formation of a capsulelike nanosized supramolecular host aggregate incorporating two guest complexes of **1** within two weakly associated half-shell cavitands.

In general, the concentration of the starting materials plays a decisive role in the formation of either insoluble polymers (concentrations > 15 mmol L^{-1}) or spherical soluble products (concentrations < 15 mmol L^{-1}). Moreover, the nature of the halide influences the formation of different polymers (2D for X = Br, I: 1,2,4 coordination mode of *cyclo*-P_5 ring of **1** (**A**, Figure 1 a) and 1D for X = Cl: 1,2 coordination mode (**B**, Figure 1 a)) and of the 90-vertex ball **1**@[{**1**}$_{12}${CuX}$_{10}${Cu_2X_3}$_5${Cu(CH_3CN)$_2$}$_5$] (**2a**: X = Cl, **2b**: X = Br; Figure 1 b). The latter structure was found for X = Cl and Br, whereas no spherical molecule was obtained for X = I. These observations raised questions over the role of other reaction parameters, solvent, and stoichiometry. In previous reports, solvent mixtures of CH_3CN and CH_2Cl_2 were used to apply a CuX/**1** stoichiometry of 2:1, which was preserved in the composition of the products. In host–guest controlled formation of spherical molecules with 99 or 80 non-carbon core atoms, the solubility of the C_{60} and *o*-carborane templates was increased by using *o*-$Cl_2C_6H_4$ instead of CH_2Cl_2.[9d,e]

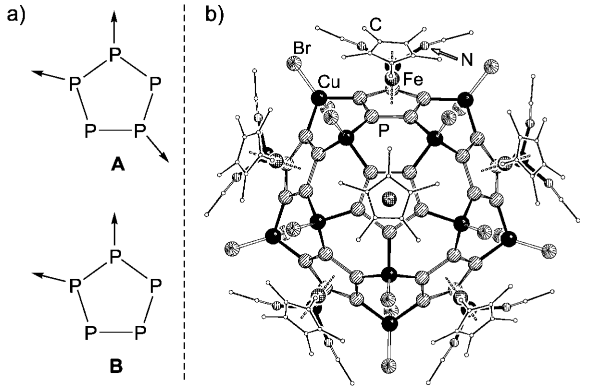

Figure 1. a) Coordination modes of **1** in CuX (X = Cl, Br, I) 1D and 2D polymers; b) spherical 90-vertex aggregate **2b** (one hemisphere obscures the other).[15]

To address the influence of stoichiometry and solvents on the formation of spherical structures, a solution of **1** in toluene was layered with a solution of CuCl in CH_3CN with a CuCl/**1**

---

[*] S. Welsch, Dr. C. Gröger, Prof. Dr. M. Scheer
Institut für Anorganische Chemie, Universität Regensburg
93040 Regensburg (Germany)
Fax: (+49) 941-943-4439
E-mail: manfred.scheer@chemie.uni-regensburg.de
Dr. M. Sierka
Institut für Chemie, Humboldt-Universität zu Berlin
10099 Berlin (Germany)

[**] This work was supported by the Deutsche Forschungsgemeinschaft. We thank Dr. M. Neumaier and Prof. Dr. H. Schnöckel for the measurement of the CSI mass spectrum. SW thanks the Fonds der Chemischen Industrie for a PhD fellowship. The COST action CM0802 PhoSciNet is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201005910.

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

stoichiometry of 2:1. Thus, we obtained the hitherto unreported 2D coordination polymer **3**, which shows a 1,2,4 coordination mode **A** (Figure 1 a), together with the spherical molecule **2a**, which then redissolves to finally form **3**. However, by using the same mixture of toluene and CH_3CN and applying a smaller amount of CuCl, namely the inverse CuCl/**1** ratio of 1:2, the additional formation of black crystals of the new compound **4**, which crystallizes at the phase boundary at the beginning of the diffusion reaction, was observed. The reduced proportion of CuCl is reflected in the composition of the product, which is now 1:1 (CuCl/**1**) and not 2:1 as found in the previously obtained spheres. Moreover, in contrast to **2**, the formation of **4** is also observed when working with concentrations greater than 15 $\mathrm{mmol\,L^{-1}}$.

A single-crystal X-ray diffraction analysis[10] showed that **4** is a capsulelike giant molecule (Figure 2). Compound **4** crystallizes in the $P2_1/n$ space group of the monoclinic crystal system and consists of two hemispheres each containing 10 CuCl units and 9 molecules of **1**. In contrast to the fivefold symmetry of the half-shells of **2** and related compounds,[9a,b,f] the half-shells in **4** possess a threefold symmetry (Figure 2 b and Figure S3). A central CuCl unit is surrounded by three moieties of **1** that exhibit a 1,2,3,4,5 coordination mode and coordinate nine further CuCl units. The upper rim of the half-shells is formed by three complexes of **1** in a 1,2,3 coordination mode and three other complexes of **1** in a 1,2 coordination mode. Overall, the half-shells consist of 9 *cyclo*-P_5 rings and 12 Cu_2P_4 six-membered rings in the boat conformation. The isolated pentagon rule is fulfilled and each Cu^I ion is coordinated in a tetrahedral fashion by one chloro ligand and three P atoms of **1**. The two half-shells of **4** are held together in the solid state by weak dispersion interactions that lead to a capsular aggregate with a skeleton of 110 inorganic core atoms, with outer dimensions of (3.0 × 2.3) nm and inner dimensions of (1.5 × 0.8) nm (Figure 2 a and Figure S2).[11] Two complexes of **1** are incorporated in this nanocapsule; these complexes presumably act as a template during the formation process (Figure 2 a). Interestingly, six cavities can be identified in the junction between the hemispheres, and toluene solvent molecules perfectly fit into these pores (Figure S6). The P–P bond lengths in the coordination network of **4** are between 2.094(3) Å and 2.126(3) Å. These bond lengths are slightly longer than in the ball-shaped aggregate **2a** (2.072(6) Å–2.122(6) Å)[9a] and the inorganic C_{80} analogue $C_2B_{10}H_{12}@[(\mathbf{1})_{12}(CuCl)_{20}]$ (**5**; 2.086(5)–2.103(4) Å).[9e] However, the average P–P distance of 2.108(3) Å in **4** is shorter than that found in the free ligand **1** (2.120(2) Å).[7c] The Cu–P distances (2.283(2)–2.335(2) Å) in **4** are somewhat longer than those of **2a** (2.264(5)–2.319(5) Å) and **5** (2.282(3)–2.307(4) Å). The two guest molecules in the different half-shells show π stacking with a minimum C–C distance of 3.64(2) Å (Figure S5a).[12]

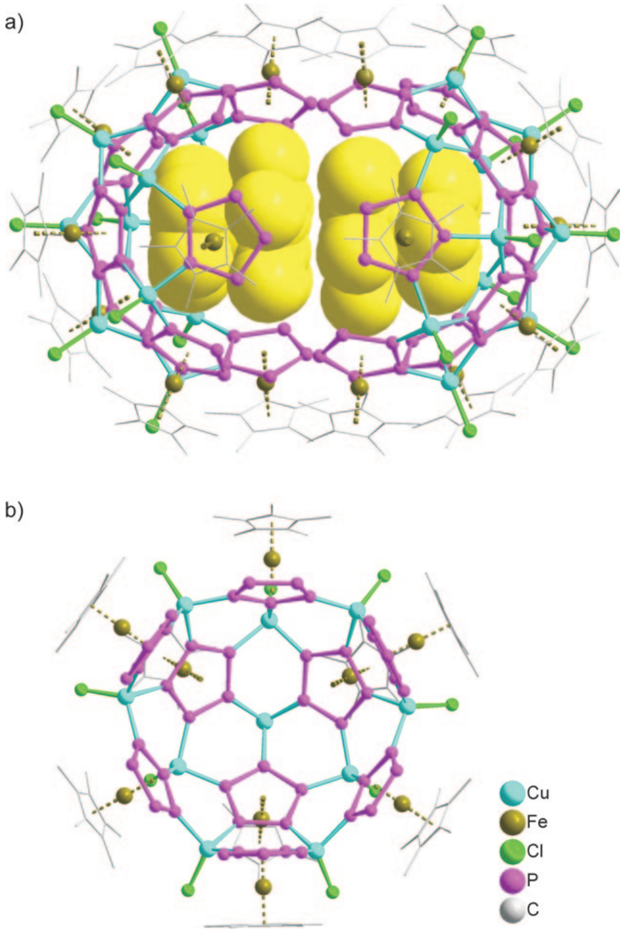

Figure 2. a) Molecular structure of **4** in the solid state (space-filling model for the endohedral complexes **1**; ball-and-stick model for the inorganic host molecule); H atoms are omitted for clarity. b) View of one half-shell of **4** (without guest molecule) illustrating the threefold symmetry.

Unlike the $[Cp^*FeP_5]$ guest molecules in **2** and related compounds,[9a,f] the encapsulated units of **1** in **4** show no *cyclo*-P_5···*cyclo*-P_5 contacts with the complexes of **1** in the host. In addition to the π stacking between the endohedral complexes, the capsules are interlinked in the solid state by eight Cp*···Cl and four Cp*···Cp* contacts (Figure S4). The centroids of the organometallic host–guest complexes thereby form an A-centered packing motif (Figure S5b).

The 2D polymeric compound **3** crystallizes in the form of brown platelike single crystals in the $P\bar{4}2_1c$ space group of the tetragonal crystal system.[10] Each Cu^I ion in **3** shows a tetrahedral coordination environment with one chloro and three pentaphosphaferrocene ligands (Figure 3, Figure S1). The $\eta^5{:}\eta^1{:}\eta^1{:}\eta^1$ coordination mode of the *cyclo*-P_5 ligands of **1**, with bonds to copper ions from the 1-, 2-, and 4-positions, leads to the formation of undulating 2D sheets. These sheets contain an inorganic backbone of Cu_2P_4 rings in the boat conformation (folding angle 23.72(1)°) and Cu_4P_{12} rings. The P–P bond lengths (2.099(1)–2.108(1) Å) of the insoluble compound are, within the standard deviations, identical to the corresponding bond lengths in the isotypic CuBr analogue[8] and slightly shorter than in **4**, the CuCl 1D polymer (2.109(2)–2.124(1) Å),[8] and the free ligand **1** (2.120(2) Å).[7c]

The nanosized capsule **4** is insoluble in solvents such as CH_2Cl_2, toluene, or *n*-alkanes. In the more polar solvent CH_3CN, the compound is sparingly soluble and degradation of the capsular structure occurs. In the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **4**, free **1** was observed. In the high-resolution cold-spray ionization (CSI) mass spectrum of a solution of **4** in

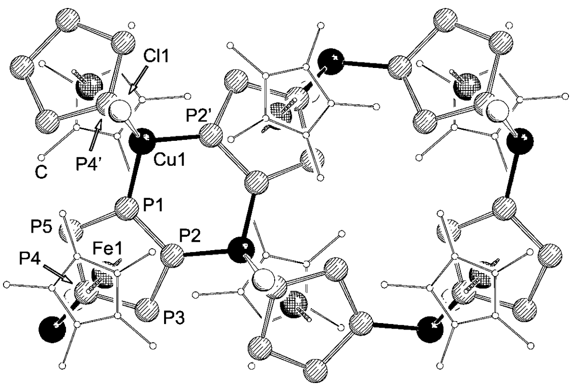

Figure 3. Section of the 2D polymeric network of **3**; viewing direction along the crystallographic *c* axis (H atoms are omitted for clarity).[15] Selected bond lengths [Å] and angles [°]: P1–P2 2.0994(6), P2–P3 2.1006(7), P3–P4 2.1054(7), P4–P5 2.1072(7), P5–P1 2.1079(7), Cu1–P1 2.2760(4), Cu1–P2′ 2.2754(4), Cu1–P4′ 2.3230(5), Cu1–Cl1 2.2159(5); P1-Cu1-P2′ 103.07(2), P1-Cu1-P4′ 101.86(2), P2′-Cu1-P4′ 102.89(2).

CH_3CN, a large number of degradation and reaggregation products of the half-shells were unambiguously identified, including ions such as $[(\mathbf{1})_4(CuCl)_9Cu]^+$. The solid-state $^{31}P\{^1H\}$ MAS NMR spectrum of **4** shows a group of broad superimposed signals in the range between 40 ppm and 180 ppm.[13]

Density functional theory calculations, including empirical dispersion correction (DFT + D), were performed in order to elucidate the nature of the interactions in **4**. Full structure optimization results in only negligible deviations from the experimental geometry. For the analysis of the interactions within **4**, we consider three hypothetical processes: I) formation of **4** from two half-shells, each containing one guest molecule [Cp*FeP$_5$], II) formation of **4** from the host molecule and the guest complex of two molecules of **1**, and III) formation of the guest complex from two isolated molecules of **1**. Table 1 shows the corresponding reaction energies and their decomposition into the DFT and dispersion contributions. All energies were obtained from single-point calculations of the structure of **4**.

In addition, to test the reliability of the DFT + D approach, we also evaluated the reaction energy for reaction III by using the MP2 method. The calculated energy is $-35.1\ \mathrm{kJ\,mol^{-1}}$, which is in excellent agreement with the DFT + D result. The results presented in Table 1 demonstrate that dispersion interactions are the sole force responsible for holding together the two half-shells in **4**. The pure DFT contributions, which include electrostatic but not dispersion interactions, are strictly repulsive. Reaction I can be regarded as the "intramolecular adhesion energy" between the two half-shells of **4**. The value of $-268\ \mathrm{kJ\,mol^{-1}}$ may seem large, but if it is divided by the contact area (ca. 290 Å^2), a value of about $-0.92\ \mathrm{kJ\,mol^{-1}\,Å^{-2}}$ is obtained. This value is smaller than, for example, that of graphite ($-3.14\ \mathrm{kJ\,mol^{-1}\,Å^{-2}}$).[14]

Table 1: Calculated DFT + D interaction energies [kJ mol^{-1}] between different parts of **4**, according to reactions I–III. The energies are divided into the pure DFT contributions (using SVP and TZVP basis sets, DFT/TZVP, and DFT/SVP, respectively) and dispersion correction (D).

Reaction	DFT + D	DFT/TZVP[a]	DFT/SVP[a]	D
I	−268.0	192.9 (174.9)	203.8 (108.6)	−460.9
II	−453.8	248.8 (209.0)	256.9 (66.6)	−702.6
III	−36.7	35.9 (33.9)	36.9 (28.1)	−72.6

[a] Energy values without BSSE correction are given in parentheses.

In conclusion, a new 2D coordination polymer **3** and a capsular organometallic giant molecule **4** were shown to be accessible by modification of the conditions of the reaction between CuCl and [Cp*FeP$_5$] (**1**). Compound **4** consists of two half-shells that are formed from a threefold symmetric starting point of aggregation and encapsulate two molecules of complex **1**. Four different coordination modes of **1** are observed, that is two, three, and fivefold, and no coordination, within one compound. DFT calculations on **4** revealed that this host–guest system is assembled exclusively by weak dispersion interactions—a feature that was not reported to date in inorganic or organometallic capsular compounds. The results provide a striking demonstration of how small changes in reaction conditions can have a decisive impact on complex supramolecular self-assembly processes.

Received: September 20, 2010
Published online: January 5, 2011

Keywords: capsules · host–guest systems · phosphorus · self-assembly · supramolecular chemistry

---

[1] a) C. J. Jones, *Chem. Soc. Rev.* **1998**, *27*, 289–299; b) G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, *100*, 3483–3537; c) S. Leininger, B. Olenyuk. P. J. Stang, *Chem. Rev.* **2000**, *100*, 853–908; d) G. F. Swiegers, T. J. Malefetse, *Coord. Chem. Rev.* **2002**, *225*, 91–121; e) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972–983; f) M. Fujita, M. Tominaga, A. Hori, B Therrien, *Acc. Chem. Res.* **2005**, *38*, 371–380; g) C. Schmuck, *Angew. Chem.* **2007**, *119*, 5932–5935; *Angew. Chem. Int. Ed.* **2007**, *46*, 5830–5833; h) S. J. Dalgarno, N. P. Power, J. L. Atwood, *Coord. Chem. Rev.* **2008**, *252*, 825–841; i) E. C. Constable, *Coord. Chem. Rev.* **2008**, *252*, 842–855; j) J. Rebek, Jr., *Acc. Chem. Res.* **2009**, *42*, 1660–1668; k) M. Yoshizawa, J. K. Klosterman, M. Fujita, *Angew. Chem.* **2009**, *121*, 3470–3490; *Angew. Chem. Int. Ed.* **2009**, *48*, 3418–3438.

[2] a) V. M. Dong, D. Fielder, B. Carl, R. B. Berg, K. N. Raymond, *J. Am. Chem. Soc.* **2006**, *128*, 14464–14465; b) N. P. Power, S. J. Dalgarno, J. L. Atwood, *Angew. Chem.* **2007**, *119*, 8755–8758; *Angew. Chem. Int. Ed.* **2007**, *46*, 8601–8604; c) D. Ajami, J. Rebek, Jr., *Angew. Chem.* **2007**, *119*, 9443–9446; *Angew. Chem. Int. Ed.* **2007**, *46*, 9283–9286; d) D. Ajami, J. Rebek, Jr., *Angew. Chem.* **2008**, *120*, 6148–6150; *Angew. Chem. Int. Ed.* **2008**, *47*, 6059–6061; e) P. Jin, S. J. Dalgarno, C. Barnes. S. J. Teat, J. L. Atwood, *J. Am. Chem. Soc.* **2008**, *130*, 17262–17263; f) P. Mal, B. Breiner, R. Rissanen, J. R. Nitschke, *Science* **2009**, *324*, 1697–1699; g) M. Mastalerz, *Angew. Chem.* **2010**, *122*, 5164–5175; *Angew. Chem. Int. Ed.* **2010**, *49*, 5042–5053.

[3] a) S. J. Dalgano, S. A. Tucker, D. B. Bassil, J. L. Atwood, *Science* **2005**, *309*, 2037–2039; b) S. Hiraoka, K. Harano, T. Nakamura, M. Shiro, M. Shionoya, *Angew. Chem.* **2009**, *121*, 7140–7143; *Angew. Chem. Int. Ed.* **2009**, *48*, 7006–7009.

[4] a) A. Müller, P. Kögerler, A. W. M. Dress, *Coord. Chem. Rev.* **2001**, *222*, 193–218; b) J. M. Breen, W. Schmitt, *Angew. Chem.* **2008**, *120*, 7010–7014; *Angew. Chem. Int. Ed.* **2008**, *47*, 6904–

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

6908; c) D.-L. Long, R. Tsunashima, L. Cronin, *Angew. Chem.* **2010**, *122*, 1780 – 1803; *Angew. Chem. Int. Ed.* **2010**, *49*, 1736 – 1758; d) A. M. Todea, A. Merca, H. Bögge, T. Glaser, J. M. Pigga, M. L. K. Langston, T. Liu, R. Prozorov, M. Luban, C. Schröder, W. H. Casey, A. Müller, *Angew. Chem.* **2010**, *122*, 524 – 529; *Angew. Chem. Int. Ed.* **2010**, *49*, 514 – 519.

[5] Z. H. Fard, M. R. Halvagar, S. Dehnen, *J. Am. Chem. Soc.* **2010**, *132*, 2848 – 2849.

[6] a) C. Schäffer, H. Bögge, A. Merca, I. A. Weinstock, D. Rehder, E. T. K. Haupt, A. Müller, *Angew. Chem.* **2009**, *121*, 8195 – 8200; *Angew. Chem. Int. Ed.* **2009**, *48*, 8051 – 8056.

[7] a) O. J. Scherer, T. Brück, *Angew. Chem.* **1987**, *99*, 59; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 59; b) O. J. Scherer, T. Brück, G. Wolmershäuser, *Chem. Ber.* **1988**, *121*, 935 – 938; c) M. Scheer, L. J. Gregoriades, A. V. Virovets, W. Kunz, R. Neueder, I. Krossing, *Angew. Chem.* **2006**, *118*, 5818 – 5822; *Angew. Chem. Int. Ed.* **2006**, *45*, 5689 – 5693; d) F. Dielmann, R. Merkle, S. Heinl, M. Scheer, *Z. Naturforsch.* **2009**, *64b*, 3 – 10.

[8] J. Bai, A. V. Virovets, M. Scheer, *Angew. Chem.* **2002**, *114*, 1808 – 1811; *Angew. Chem. Int. Ed.* **2002**, *41*, 1737 – 1740.

[9] a) J. Bai, A. V. Virovets, M. Scheer, *Science* **2003**, *300*, 781 – 783; b) M. Scheer, J. Bai, B. P. Johnson, R. Merkle, A. V. Virovets, C. E. Anson, *Eur. J. Inorg. Chem.* **2005**, 4023 – 4026; c) B. P. Johnson, F. Dielmann, G. Balázs, M. Sierka, M. Scheer, *Angew. Chem.* **2006**, *118*, 2533 – 2536; *Angew. Chem. Int. Ed.* **2006**, *45*, 2473 – 2475; d) 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; e) M. Scheer, A. Schindler, C. Gröger, A. V. Virovets, E. V. Peresypkina, *Angew. Chem.* **2009**, *121*, 5148 – 5151; *Angew. Chem. Int. Ed.* **2009**, *48*, 5046 – 5049; f) M. Scheer, A. Schindler, J. Bai, B. P. Johnson, R. Merkle, R. Winter, A. V. Virovets, E. V. Peresypkina, V. A. Blatov, M. Sierka, H. Eckert, *Chem. Eur. J.* **2010**, *16*, 2092 – 2107.

[10] See the Supporting Information for details of the X-ray structure analyses.

[11] The outer diameters were calculated from the H–H distances of the methyl H atoms plus two times the van der Waals radius of the H atom (0.12 nm). The inner diameters were analogously calculated as P–P distances minus two times the van der Waals radius of the P atom (0.18 nm).

[12] In the crystal lattice, the endohedral [Cp*FeP$_5$] complexes show a disorder over two positions, both of which exhibit π stacking.

[13] The calculated MAS NMR spectrum of **4** is consistent with the observed signal range. However, the simultaneous presence of **3** in the MAS sample cannot be definitely excluded from experimental data because of the broadness of the signals and the similar chemical shifts.

[14] T. Kerber, M. Sierka, J. Sauer, *J. Comput. Chem.* **2008**, *29*, 2088 – 2097.

[15] The drawings were generated with the SCHAKAL 99 software by E. Keller, Albert-Ludwigs-Universität Freiburg, Germany: E. Keller, *Chem. Unserer Zeit* **1980**, *14*, 56 – 60.

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim