Fullerene-Like Nanoballs Formed by Pentaphosphaferrocene and CuBr

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Dedicated to Professor H. W. Roesky on the occasion of his 70th birthday

Keywords: Polyphosphorus ligands / Fullerene-like molecules / Iron / Phosphorus / Cluster / Nanochemistry

Reaction of [$Cp^xFe(\eta^5-P_5)$] {$Cp^x = \eta^5-C_5Me_5$ (**1a**), $\eta^5-C_5Me_4Et$ (**1b**)} with CuBr leads to the fullerene-like nanoballs [{$Cp^xFe(\eta^5:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1-P_5)$}$_{12}${CuBr}$_{10}${$Cu_2Br_3$}$_5${$Cu(CH_3CN)_2$}$_5$] {$Cp^x = \eta^5-C_5Me_5$ (**5a**), $\eta^5-C_5Me_4Et$ (**5b**)} comprising a cluster core of 90 non-carbon atoms. In contrast to previous results by variation of stoichiometry and concentration conditions, the formation of polymeric product was hindered, and exclusive formation of the spherical cage compound was achieved. The cluster **5b** possesses an inside diameter of 1.29 nm and an outside diameter of 2.37 nm. Definitive evidence for encapsulation of a [$Cp^xFe(\eta^5-P_5)$] unit (**1b**) within the inner cavity of the nanocluster **5b** is shown by X-ray crystallographic results.

Introduction

Large spherical molecules and clusters are a fascinating field in contemporary chemistry. Established areas like the borane cages have recently been augmented by the discovery of low-valent aluminium and gallium metalloid clusters,[1] and within the growing area of giant clusters the chalcogeno-bridged copper and silver clusters[2] as well as the giant polyoxomolybdates establishing wheels and balls[3] are of the largest structurally characterised clusters so far. Among others an inorganic "superfullerene" [$Mo_{132}O_{372}(CH_3CO_2)_{30}(H_2O)_{72}$]$^{42-}$ has been reported reflecting a pentagonal-shaped symmetry.[4,5] Fullerene-like molecules based on carbon-free elements exist so far only in the solid state Zintl phases $Na_{172}In_{197}M_2$ (M = Ni, Pd, or Pt) with a C_{60}-like polyhedron of $In_{48}Na_{12}$ moieties, whereas an In_{74} fullerene-like unit with D_{3h} symmetry was found within $Na_{96}In_{97}M_2$.[6,7]

Within our efforts to study the coordination chemistry of naked P_n ligand complexes to form well-oriented supramolecular assemblies as well as one-dimensional (1D) and two-dimensional (2D) polymers, we used pentaphosphaferrocene **1a** as a starting material. Thus, the reaction of **1a** with Cu^I bromide and iodide led to the quantitative formation of 2D polymeric frameworks of **2a**,**b**.[8] However, when CuCl was used, the reaction yielded **3** as a linear 1D polymer in a maximum of about 50% yield.[8] As the soluble product of the latter reaction complex **4** was formed revealing a spherical fullerene-like molecule containing 90 non-carbon core atoms.[9] In continuation of these investigations the question arises whether it would be possible selectively to obtain such soluble nano-scaled spherical aggregates for the other Cu^I halides. We have now found that depending on the stoichiometry of the starting materials and the concentration conditions it is possible to obtain exclusively soluble spherical molecules of the formula [{$Cp^xFe(\eta^5:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1-P_5)$}$_{12}${CuBr}$_{10}${$Cu_2Br_3$}$_5${$Cu(CH_3CN)_2$}$_5$] {$Cp^x = \eta^5-C_5Me_5$ (**5a**), $\eta^5-C_5Me_4Et$ (**5b**)} by the reaction of **1a,b** with CuBr. This fullerene-like molecule possesses 90 non-carbon atoms. Furthermore, for the first time we have structural evidence of the existence of encapsulated molecules of **1b** in the ball of **5b**, results we are reporting herein.[10]

[$Cp^xFe(\eta^5-P_5)$] {$Cp^x = \eta^5-C_5Me_5$ (**1a**), $\eta^5-C_5Me_4Et$ (**1b**)}
[$CuX\{Cp^*Fe(\eta^5:\eta^1:\eta^1:\eta^1-P_5)\}]_\infty$ (**2a**: X = Br, **2b**: X = I)
[$CuCl\{Cp^*Fe(\eta^5:\eta^1:\eta^1-P_5)\}]_\infty$ (**3**)

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DOI: 10.1002/ejic.200500616

$[\{Cp^*Fe(\eta^5{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\eta^1\text{-}P_5)\}_{12}\{CuCl\}_{10}\{Cu_2Cl_3\}_5\{Cu(CH_3CN)_2\}_5]$ (**4**)

Results and Discussion

Complexes **5a,b** were obtained by the reaction of **1a,b** with CuBr in mixed solvents of CH_3CN and CH_2Cl_2 at ambient temperature. In comparison with the reactions leading to the 2D polymers **2a**,[8] the increase of the dilution (15 mmol/L to 7.5 mmol/L)[11] leads to the formation of the soluble products. However the polymer **2a** is still formed in yields up to 50%. With a more dilute solution (3.75 mmol/L) coupled with a stoichiometry of 2:1 CuBr/**1a**, as required for the composition of the spherical molecules of **5**, the formation of polymer was essentially negligible. Using the 2:1 stoichiometry without diluting the reaction mixture from 15 mmolar still resulted in formation of significant quantities of the polymer **2a**. Thus, the decisive criteria for the exclusive (polymer-free) formation of **5** are both the correct stoichiometry of 2:1 and a larger dilution of the reaction components ($\leq$ 3.75 mmol/L).

The black crystals of **5a**,**b** are stable under nitrogen and soluble in mixtures of CH_2Cl_2/CH_3CN. They exhibit broad ^{31}P NMR chemical shifts at about 66 and 68 ppm, respectively.

5b has been characterised by X-ray diffraction analysis.[12] The unit cell contains two crystallographically independent molecules of **5b** both lying on the mirror plane of the space group *Cm*. The molecular structure of **5b** is similar to the chlorine analog **4** (Figure 1).[9] All P atoms of the *cyclo*-P_5 ring of $[Cp^xFe(\eta^5\text{-}P_5)]$ coordinate to the copper atoms of CuBr, which are further coordinated by P atoms of other *cyclo*-P_5 rings, leading to the formation of six-membered P_4Cu_2 rings around the central *cyclo*-P_5 ring (Figure 1, a). The five- and six-membered ring alternation is similar to that seen in the fullerenes, with the difference that due to the distorted tetrahedral coordination sphere of the Cu^I ions, the six-membered rings are not planar and folded along the Cu···Cu axis (folding angle between 132.7 and 141.9°). The thus formed pseudo-hemispherical $[Cu_{10}Br_{10}\{Cp^xFe(\eta^5\text{-}P_5)\}_6]$ half-shells (Figure 1, a) are joined by five $[Cu_2Br_3]^-$ as well as by five $[Cu(CH_3CN)_2]^+$ units (Figure 1, b). Thus, ideal symmetry of the $[Cu_{25}Br_{25}(FeP_5)_{12}]$ core, consisting of 90 non-carbon atoms, is D_{5h} but the presence of ethyl groups at the cyclopentadienyl ligands reduces symmetry of the whole molecule to C_s or even C_1. All copper atoms have a tetrahedral P_3Br, P_2Br_2 or P_2N_2 environment. The Cu–Br bond lengths are 2.328(3)–2.379(3) Å (av. 2.351 Å) and 2.446(3)–2.472(4) Å (av. 2.462 Å) for terminal and bridging Br atoms, respectively. All *cyclo*-P_5 rings are nearly planar. The P–P distances, varying from 2.075(8) to 2.130(5) Å (av. 2.102 Å), are in good agreement with 2.088(3)–2.108(3) Å (av. 2.096 Å) found for the starting material **1b**.[13] The Cu–P bonds vary from 2.284(4) to 2.324(7) Å (av. 2.304 Å). This is also in good agreement with the values found in **4**

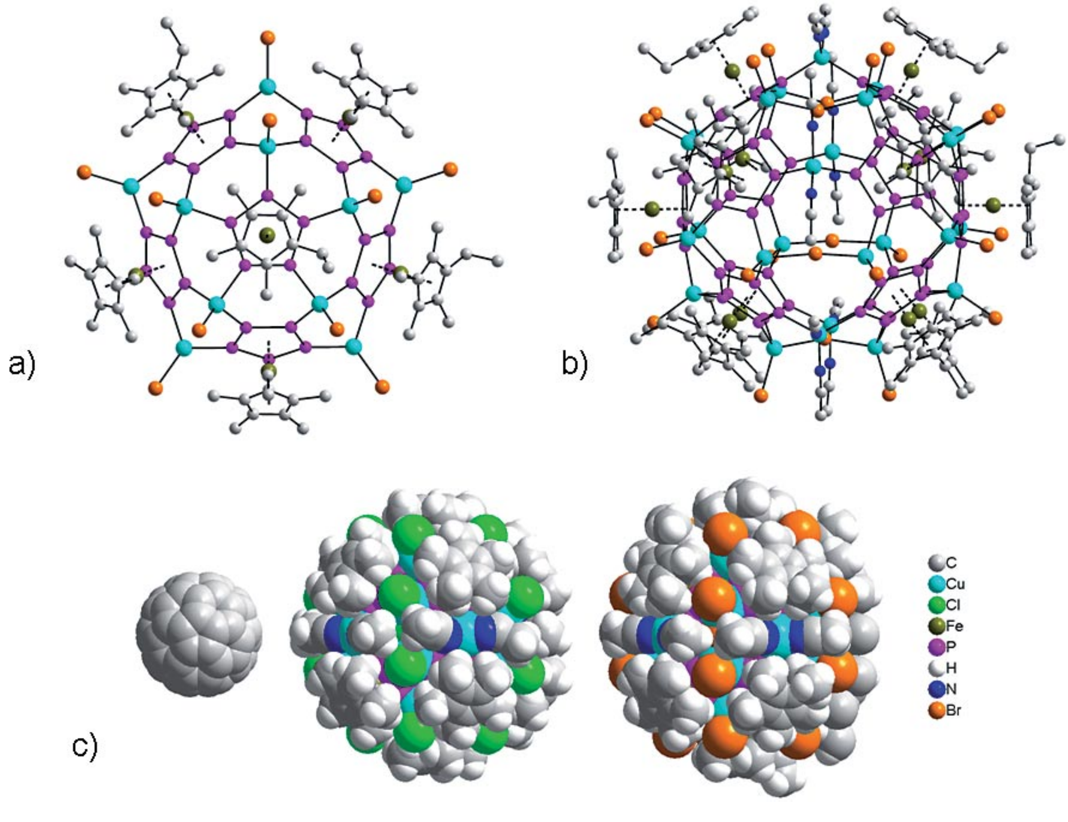

Figure 1. a) View of a half shell of a molecule of **5b**; b) Complete ball-and-stick structure of a molecule of **5b**; c) Size comparison of the spherical molecules of C_{60}, **4** and **5b** (space-filing model).

[2.294(6)–2.353(6) Å].[9] Due to the longer Cu–Br–Cu bridges [compare **4**: 2.294(6)–2.353(6) Å], which link the two half shells together, and the presence of Et groups at the Cp^x ligands the spherical body of **5b** is in comparison with **4** slightly larger and more elongated. It possesses an inside diameter of 12.9 Å (**4**: 12.2 Å) and an outside diameter of 21.4/23.7 Å (**4**: 21.4 Å), which is about three times larger than that of C_{60} (Figure 1, c).[14] Whereas for **4** we had only weak experimental data for the existence of an encapsulated $[Cp^*Fe(\eta^5\text{-}P_5)]$ (**1a**) moiety in every second ball, in **5b** we have much better structural data for the existence of an encapsulated molecule **1b** in each ball of **5b**, which is disordered in two directions with no special preference to the five-membered rings of the half-shells.

The results have shown that both stochiometry and dilution conditions are decisive for the exclusive formation of non-carbon containing nanoballs. Thus, while heterofullerenes are known containing only a few boron, nitrogen[15] and phosphorus atoms,[16] the complexes **4** and **5** exhibit a complete heteroatom composition and therefore represent a novel class of fullerene-like molecules.

Experimental Section

General Remarks: All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk techniques. All solvents were dried using standard procedures and distilled freshly before use. $[Cp^xFe(\eta^5\text{-}P_5)]$ $\{Cp^x = \eta^5\text{-}C_5Me_5$ (**1a**), $\eta^5\text{-}C_5Me_4Et$ (**1b**)$\}$[13] were prepared according to the literature.

$[\{Cp^xFe(\eta^5:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1\text{-}P_5)\}_{12}\{CuBr\}_{10}\{Cu_2Br_3\}_5\{Cu(CH_3CN)_2\}_5]$ $\{Cp^x = \eta^5\text{-}C_5Me_5$ (5a), $\eta^5\text{-}C_5Me_4Et$ (5b)$\}$: A solution of CuBr (21.5 mg, 0.15 mmol) in 5 mL of CH_3CN and 5 mL of CH_2Cl_2 was layered onto a solution of $[Cp^xFe(\eta^5\text{-}P_5)]$ (**1a**: 26 mg, 0.075 mmol; **1b**: 27 mg, 0.075 mmol) in 10 mL of CH_2Cl_2 at room temperature. After complete diffusion of the phases (about one week), the solution was decanted into a fresh Schlenk tube and layered with 20 mL of hexane. This mixture was kept for two further weeks and black crystals of **5** were formed. The mother liquor was decanted and the obtained black crystals were dried under high vacuum. **5a**: 10 mg, 20% (based on **1a**); **5b**: 8 mg, 15% (based on **1b**).

5a: $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 300 K): $\delta = 66$ ppm (br., $\omega_{1/2} = 1000$ Hz).

5b: $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 300 K): $\delta = 68$ ppm (br., $\omega_{1/2} = 850$ Hz).

Acknowledgments

This work was comprehensively supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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[10] Several intensive attempts to obtain soluble products with CuI failed.

[11] Concentrations discussed here refer to the overall concentrations of complexes **1**, as calculated using the total volume obtained after layering with the CuBr solutions.

[12] Since the single crystals of **5a** unfortunately proved to be very weakly diffracting, only the unit cell could be roughly determined at $T = 100$ K as a monoclinic unit cell with: $a = 23.22(6)$ Å, $b = 23.21(6)$ Å, $c = 31.67(5)$ Å, $\beta = 91.32(10)$, $V = 17138\ (105)$ Å^3. Crystal structure analysis of a single crystal of **5b** was carried out at 100 K on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The data were corrected for absorption using the SADABS program.[17a] The structure was solved by direct methods and refined by full-matrix least-squares methods using SHELX-97 program set.[17b]
$\{(Cp^xFeP_5)\subset[Cu_{25}Br_{25}(Cp^xFeP_5)_{12}(CH_3CN)_{10}]\}\cdot 0.5CH_3CN\cdot 2CH_2Cl_2$ ($Cp^x = \eta^5\text{-}C_5Me_4Et$): $C_{166}H_{256.5}Br_{25}Cl_4Cu_{25}Fe_{13}N_{10.5}P_{65}$, $M = 8866.47$, crystal dimensions $0.30 \times 0.25 \times 0.08$ mm^3, monoclinic, space group *Cm* (No. 8), $a = 37.4766(14)$ Å, $b = 23.8734(9)$ Å, $c = 37.3372(14)$ Å, $\beta = 98.313(1)°$, $T = 100(1)$ K, $Z = 4$, $V = 33054(2)$ Å^3, $D_c = 1.782$ Mg/m^3, μ(Mo-K_α) = 5.524 mm^{-1}. 82792 data measured to $2\theta_{max} = 56.04°$, 68911 unique ($R_{int} = 0.0562$). 2726 parameters, $wR_2 = 0.2315$, $R_1 = 0.1141$ (all data), $R_1 = 0.0877$ [51811 with $I > 2\sigma(I)$].
There are two crystallographically independent molecules of **5b** in the unit cell both lying on mirror plane of the *Cm* space group. When all atoms of main molecules were localized the electron density ($\Delta\rho$) map contained a few peaks inside both of the spheres. Accurate analysis led us to a conclusion that each sphere contains a $[Cp^xFe(\eta^5\text{-}P_5)]$ molecule located almost in the center. Each molecule is disordered over two positions with an opposite orientation and relative shift by 2.23–2.29 Å. Two positions of Cp^x ligand are overlapped. The iron and phosphorus atoms of disordered molecules were localized directly from the $\Delta\rho$ map and refined anisotropically with variable site occupancy factors. Then the positions of disordered Cp^x ligands were fitted from an idealized model to the largest $\Delta\rho$-peaks and included into refinement with fixed coordinates and $U_{iso} = 0.04$ Å^2. The final $\Delta\rho$ map contained one CH_3CN and four CH_2Cl_2 solvent molecules outside the ball-like structure. There were also some peaks probably corresponding to severely disordered CH_2Cl_2 molecules but several attempts to include them into refinement failed. Finally the structure was refined in anisotropic approximation for all non-hydrogen atoms except for carbon atoms of disordered $[Cp^xFe(\eta^5\text{-}P_5)]$

molecules inside the balls and two CH_2Cl_2 solvent molecules. Hydrogen atoms were refined geometrically. Site occupancy factors of disordered [$Cp^xFe(\eta^5-P_5)$] molecules were set as 0.70/0.30 and 0.60/0.40.

CCDC-267819 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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Received: April 14, 2005