

# cyclo-P<sub>4</sub> Building Blocks: Achieving Non-Classical Fullerene Topology and Beyond

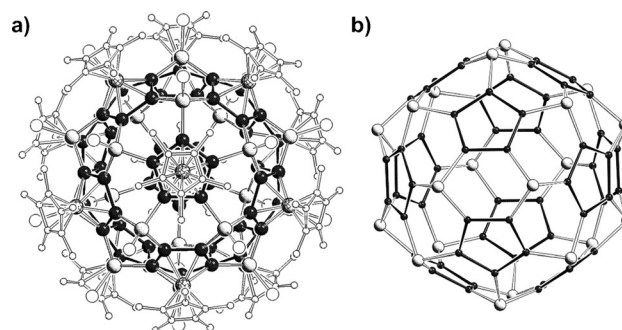
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In memory of Malcolm H. Chisholm

**Abstract:** The cyclo-P<sub>4</sub> complexes [Cp<sup>R</sup>Ta(CO)<sub>2</sub>(η<sup>4</sup>-P<sub>4</sub>)] (Cp<sup>R</sup>: Cp<sup>''</sup> = 1,3-C<sub>5</sub>H<sub>3</sub>tBu<sub>2</sub>, Cp<sup>'''</sup> = 1,2,4-C<sub>5</sub>H<sub>2</sub>tBu<sub>3</sub>) turned out to be predestined for the formation of hollow spherical supramolecules with non-classical fullerene-like topology. The resulting assemblies constructed with CuX (X = Cl, Br) showed a highly symmetric 32-vertex core of solely four- and six-membered rings. In some supramolecules, the inner cavity was occupied by an additional CuX unit. On the other hand, using CuI, two different supramolecules with either peanut- or pear-like shapes and outer diameters in the range of 2–2.5 nm were isolated. Furthermore, the spherical supramolecules containing Cp<sup>'''</sup> ligands at tantalum are soluble in CH<sub>2</sub>Cl<sub>2</sub>. NMR spectroscopic investigations in solution revealed the formation of isomeric supramolecules owing to the steric hindrance caused by the third tBu group on the Cp<sup>'''</sup> ligand. In addition, a 2D coordination polymer was obtained and structurally characterized.

Fullerenes, defined as spherical carbon clusters, are prime examples of discrete nanosized supramolecules. Owing to their unique optic and electronic properties, they have gained increasing attention in materials science and nanotechnology.<sup>[1]</sup> However, the majority of reports on fullerenes are restricted to the most stable derivatives such as C<sub>60</sub> and C<sub>70</sub>, which can be prepared on a reasonable scale. Consisting solely of five- and six-membered rings, they are so-called

classical fullerenes. Some time ago, we succeeded in showing that [Cp\*Fe(η<sup>5</sup>-P<sub>5</sub>)] (Cp\* = C<sub>5</sub>Me<sub>5</sub>) containing a cyclo-P<sub>5</sub> ligand self-assembles with copper(I) halides to give supramolecules with fullerene-like topology. These unprecedented carbon-free analogues of the I<sub>h</sub>-C<sub>80</sub> (Figure 1) and I-C<sub>140</sub> frameworks represent less stable fullerene-like congeners.<sup>[2]</sup>



**Figure 1.** a) Supramolecule with 80 vertices based on [Cp\*Fe(η<sup>5</sup>-P<sub>5</sub>)] and CuX (X = Cl, Br). b) The molecular scaffold illustrating the I<sub>h</sub>-C<sub>80</sub> fullerene topology.

Some time ago, we were interested to see whether non-classical fullerenes of various ring sizes<sup>[3]</sup> are also accessible using the metallasupramolecular approach. The cyclo-P<sub>4</sub> complex [Cp<sup>''</sup>Ta(CO)<sub>2</sub>(η<sup>4</sup>-P<sub>4</sub>)]<sup>[4]</sup> (**1a**; Cp<sup>''</sup> = 1,3-C<sub>5</sub>H<sub>3</sub>tBu<sub>2</sub>) seems to be predestined for the formation of spheres comprising the four-membered ring motif. First investigations of the reactivity of **1a** with CuCl revealed the formation of the spherical supramolecule [(Cp<sup>''</sup>Ta(CO)<sub>2</sub>(η<sup>4</sup>-P<sub>4</sub>))<sub>6</sub>{CuCl}<sub>8</sub>] (**2a**), which consists exclusively of four- and six-membered rings.<sup>[5]</sup> Its scaffold consists of 32 inorganic core atoms and exhibits O<sub>h</sub> symmetry; this non-classical fullerene framework has not been obtained in fullerene chemistry thus far.<sup>[6]</sup>

This single result led to some decisive questions as to whether the concept of structural arrangements of four- and six-membered rings in supramolecules could be extended to unprecedented spherical structural motifs as it was possible for the five-membered ring of pentaphosphaferrocene.<sup>[2,7]</sup> Moreover, further information on the formation process and the structural stability in solution was required as the insolubility of the formerly obtained 32-vertex ball **2a** did not allow for any investigations of its behavior in solution. Thus a third *tert*-butyl group was introduced into the cyclopentadienyl ring to increase the solubility, and the complex

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$[\text{Cp}^{\text{R}}\text{Ta}(\text{CO})_2(\eta^4\text{-P}_4)]$  (**1b**;  $\text{Cp}^{\text{R}} = 1,2,4\text{-C}_5\text{H}_2\text{tBu}_3$ ) was synthesized, structurally characterized, and examined in terms of its reactivity towards copper(I) halides.

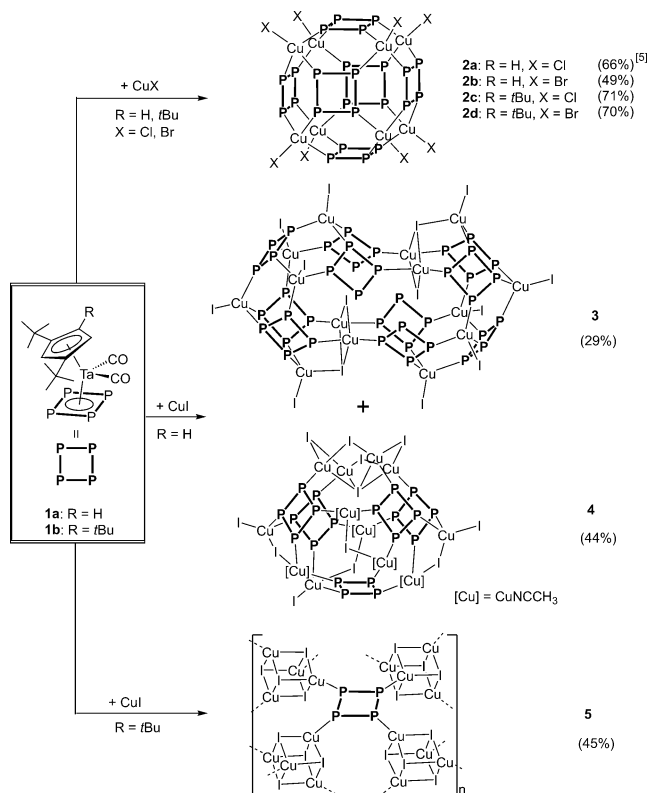
Herein, we report on a systematic investigation of the reactivity of the *cyclo*- $\text{P}_4$  ligand tantalum complexes **1a** and **1b** towards  $\text{CuX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), which led to the isolation and structural characterization of three novel representatives of spherical  $\text{C}_{32}$  analogues  $[[\text{Cp}^{\text{R}}\text{Ta}(\text{CO})_2(\eta^4\text{-P}_4)]_6\{\text{CuX}\}_8]$  (**2b**:  $\text{Cp}^{\text{R}} = \text{Cp}^{\text{H}}$ ,  $\text{X} = \text{Br}$ ; **2c**:  $\text{Cp}^{\text{R}} = \text{Cp}^{\text{tBu}}$ ,  $\text{X} = \text{Cl}$ ; **2d**:  $\text{Cp}^{\text{R}} = \text{Cp}^{\text{H}}$ ,  $\text{X} = \text{Br}$ ). For the first time, the solubility of the  $\text{Cp}^{\text{R}}$  derivatives (**2c** and **2d**) enabled a characterization in solution. Furthermore, we succeeded in the isolation of two spheres containing singular scaffolds,  $[[\text{Cp}^{\text{R}}\text{Ta}(\text{CO})_2(\eta^4\text{-P}_4)]_{10}\{\text{Cu}_{14}\text{I}_{10}(\mu\text{-I})_2(\mu_3\text{-I})_2\}]$  (**3**) and  $[[\text{Cp}^{\text{R}}\text{Ta}(\text{CO})_2(\eta^4\text{-P}_4)]_5\{\text{Cu}_{12}\text{I}_3(\mu\text{-I})_8(\mu_4\text{-I})(\text{CH}_3\text{CN})_5\}]$  (**4a**, **4b**). The unprecedented double sphere of **3** shows potential for subsequent aggregation according to the spherical building block concept. Their structures give insight into the formation pathway of the 32-vertex balls as the missing  $\text{TaP}_4$  unit is replaced by a  $\text{CuI}$  network to form **4** or is merged to a second incomplete ball via a  $(\text{CuI})_x$  moiety to form “peanut”-shaped compound **3**.

A solution of  $\text{CuBr}$  in  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  was carefully layered on a solution of **1a** in  $\text{CH}_2\text{Cl}_2$  or in a  $\text{CH}_2\text{Cl}_2/\text{DMF}$  mixture whereupon the formation of orange crystals of **2b** at the phase boundary could be observed within one day (Figure 2). **2b** crystallizes in the trigonal space group  $R\bar{3}$  as a  $\text{CH}_2\text{Cl}_2$  solvate, and its molecular structure was identified as the supramolecule  $[[\text{Cp}^{\text{R}}\text{Ta}(\text{CO})_2(\eta^4\text{-P}_4)]_6\{\text{CuBr}\}_8]$  (**2b**). Com-

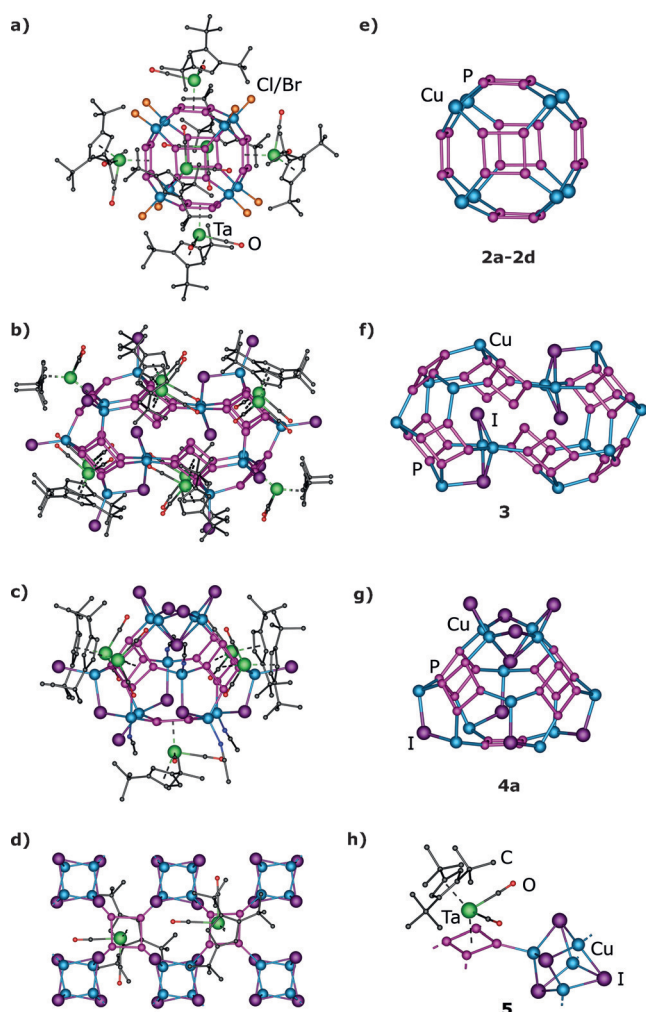
pound **2b** consists of six *cyclo*- $\text{P}_4$  complexes **1a** bound to eight copper(I) halide units in a 1,2,3,4-Coordination mode, as in the Cl derivative **2a**. Each Cu atom is tetrahedrally coordinated by three P atoms and one terminal halide. The inorganic core consists of 32 non-carbon atoms and features a  $\text{Cu}_8$  cube with *cyclo*- $\text{P}_4$  rings above its six faces. This results in a closed structure consisting exclusively of alternating four- and six-membered rings to give the topology of a truncated octahedron. Consequently, the tantalum atoms form a  $\text{Ta}_6$  octahedron.<sup>[13]</sup> The P–P bond lengths of 2.1569(15)–2.1840(15) Å in **2b** are similar to those in the free complex **1a**<sup>[4]</sup> (2.157(2)–2.189(2) Å). The inner cavity of **2b** has a diameter<sup>[8]</sup> of 0.6 nm and possesses a cuboidal shape, with the Cu atoms in the corners and the  $\text{P}_4$  rings forming the faces. The outer diameter is 2.17 nm, which is similar to that of **2a**.

A change of the used halide to iodide did not result in the formation of the isostructural  $\text{C}_{32}$  analogue as  $\text{CuI}$ , unlike other copper(I) halides, tends to form extended  $\text{CuI}$  aggregates.<sup>[9]</sup> By carefully layering a solution of  $\text{CuI}$  in  $\text{CH}_3\text{CN}$  over a solution of **1a** in toluene, orange prisms of  $[[\text{Cp}^{\text{R}}\text{Ta}(\text{CO})_2(\eta^4\text{-P}_4)]_{10}\{\text{Cu}_{14}\text{I}_{10}(\mu\text{-I})_2(\mu_3\text{-I})_2\}]$  (**3**) were formed within four days (Figure 2). After approximately two weeks, a new crop of yellow prisms appeared as the second fraction, representing another spherical cluster, namely  $[[\text{Cp}^{\text{R}}\text{Ta}(\text{CO})_2(\eta^4\text{-P}_4)]_5\{\text{Cu}_{12}\text{I}_3(\mu\text{-I})_8(\mu_4\text{-I})(\text{CH}_3\text{CN})_5\}]$  (**4**; Figure 2). The crystallization of cluster **4** was delayed during the synthesis of **3** owing to its higher solubility, which was concluded from an optical examination of the crystalline material and the unit cells of dozens of different crystals. The formation of **3** and **4** in the same reaction is due to the very similar ratios of **1a**/ $\text{CuI}$  in the composition of both products (**3**: 1:2.33; **4**: 1:2.40). Interestingly, the direct synthesis of compound **4** was possible under similar reaction conditions in the presence of  $[\text{Cp}^{\text{R}}\text{Fe}(\eta^5\text{-P}_5)]$ . The formation of **4**, albeit as another solvatomorph (**4a**), was accompanied by the formation of brown needles of the earlier reported 2D coordination polymer  $[[\text{Cp}^{\text{R}}\text{Fe}(\eta^5\text{-P}_5)](\text{CuI})]_n$ .<sup>[10]</sup> Apparently, the presence of  $[\text{Cp}^{\text{R}}\text{Fe}(\eta^5\text{-P}_5)]$  in the reaction mixture inhibits the preliminary formation of **3** and favors the formation of **4**.

Compound **3** crystallizes in the monoclinic space group  $C2/m$ , and structural analysis revealed an unprecedented nanocapsule that consisted of ten *cyclo*- $\text{P}_4$  complexes **1a** bound to eight  $\text{CuI}$  units and two  $\text{Cu}_3\text{I}_3$  units (Figure 3b). Six complexes **1a** bind in a 1,2,3,4- and four in a 1,2,3-Coordination mode. The whole supramolecule **3** can be described in terms of two  $[[\text{Cp}^{\text{R}}\text{Ta}(\text{CO})_2(\eta^4\text{-P}_4)]_5(\text{CuI})_5]$  fragments connected by two  $\text{Cu}_2\text{I}_2$  units. The two cluster fragments have similar inorganic frameworks, which can be derived from those of **2a** and **2b** by removing one *cyclo*- $\text{P}_4$  complex **1a** and coordinating four  $\text{CuX}$  units to it. Therefore, it seems that on the way to the formation of the regular 32-vertex spheres of **2**, two incomplete spheres were fused by two  $\text{Cu}_2\text{I}_2$  units to give the double sphere **3**. The resulting inner scaffold of **3** has a peanut-like shape and consists of 58 inorganic core atoms, 40 P, 14 Cu, and 4 I atoms (Figure 3). The iodine atoms only support the scaffold as its connectivity can be achieved with  $\text{Cu}$ –P bonds. As expected, the  $\text{Cu}$ –I bonds with terminal iodides (average: 2.53(1) Å) are shorter than to  $\mu\text{-I}$  (2.598(3) Å) and  $\mu_3\text{-I}$  (average: 2.69(2) Å) atoms. The P–P



**Figure 2.** Reactions of  $[\text{Cp}^{\text{R}}\text{Ta}(\text{CO})_2(\eta^4\text{-P}_4)]$  (**1a**:  $\text{Cp}^{\text{R}} = \text{Cp}^{\text{H}}$ ; **1b**:  $\text{Cp}^{\text{R}} = \text{Cp}^{\text{tBu}}$ ) with copper(I) halides yield the supramolecules **2–4** and the coordination polymer **5** (yields in parentheses).



**Figure 3.** a–c) Molecular structures of **2c** (a), **3** (b), and **4a** (c). d) Section of the 2D polymeric network in **5**. Hydrogen atoms omitted for clarity. e–g) Scaffolds of the supramolecules **2a–d** (e), **3** (f), and **4a** (g). h) Repeating unit of **5**.

bond lengths of 2.138(5)–2.191(5) Å in **3** are in a wider range than in the free complex **1a**.<sup>[4]</sup> The supramolecule **3** has a long axis<sup>[8]</sup> of 2.81 nm and a short axis of 2.28 nm. The inner cavity of **3** is completely blocked by the  $\mu$ -I atoms of the  $\text{Cu}_3\text{I}$  units.<sup>[13]</sup>

Compound **4** crystallizes as two solvatomorphic forms, the orthorhombic (space group  $Pbca$ , **4a**) and the monoclinic (space group  $P2_1/n$ , **4b**) form. Single-crystal X-ray diffraction manifested the presence of a hollow shell in both cases, which consisted of five *cyclo*- $\text{P}_4$  complexes **1a** bound to three neutral  $\{\text{Cu}_2\text{I}_2\text{CH}_3\text{CN}\}$  units, one cationic  $\{\text{Cu}_2\text{I}(\text{CH}_3\text{CN})_2\}^+$ , and one anionic  $\{\text{Cu}_4\text{I}_5\}^-$  unit (Figure 3c). Complex **1a** features a 1,2,3,4-coordination mode just like clusters **2a** and **2b**, but the different nature of the copper halide units leads to a completely new framework. The inorganic scaffold of **4** can be described as an open shell of five *cyclo*- $\text{P}_4$  rings connected via eight  $\text{Cu}_2(\mu\text{-I})$  units, which form four five-membered  $\text{P}_2\text{Cu}_2\text{I}$  and four eight-membered  $\text{P}_4\text{Cu}_3\text{I}$  rings. The open shell is capped by a bowl-like  $\{\text{Cu}_4\text{I}_5\}^-$  unit (Figure 3g), a common building unit in CuBr- and CuI-based supramolecules.<sup>[2d,f,7]</sup> In

**4**, in contrast to **3**, iodide becomes a part of the inorganic scaffold of **4** that consists of 41 core atoms (20 P, 12 Cu, 9 I) and has  $C_2$  symmetry. Each Cu atom in **4** is tetracoordinated, and the Cu–I bond lengths of terminal iodides (average: 2.55(1) Å in **4a**, 2.56(1) Å in **4b**) are typically shorter than to  $\mu$ -I atoms (2.6(1) Å in **4a**, 2.64(8) Å in **4b**). The P–P bonds in **4a** (2.129(3)–2.168(3) Å) and **4b** (2.128(4)–2.166(4) Å) are shorter than in **1a** and **3**, respectively. The spherical cluster **4** has an outer diameter<sup>[8]</sup> of 2.35 nm. Like in **3**, the inner cavity of **4** is occupied by iodide, which here belongs to the  $\{\text{Cu}_4\text{I}_5\}^-$  unit. Interestingly, the supramolecules **4a** and **4b** are isomers: The structural difference between their scaffolds was traced back to two positions occupied by either an iodide or a  $\text{CH}_3\text{CN}$  molecule.<sup>[13]</sup>

In the IR spectra of all products, the two CO stretching vibrations (**2a**: 2040  $\text{cm}^{-1}$ , 1974  $\text{cm}^{-1}$ ; **2b**: 2042  $\text{cm}^{-1}$ , 1972  $\text{cm}^{-1}$ ; **3**: 2011  $\text{cm}^{-1}$ , 1969  $\text{cm}^{-1}$ ; and **4**: 2017  $\text{cm}^{-1}$ , 1976  $\text{cm}^{-1}$ ) all display a significant shift to higher wavenumbers compared to those of **1a** (1983  $\text{cm}^{-1}$ , 1952  $\text{cm}^{-1}$ ). Furthermore, all compounds obtained from the  $\text{Cp}''$  derivative **1a** were completely insoluble in *n*-hexane, toluene,  $\text{CH}_2\text{Cl}_2$ , and THF.

Certainly, NMR spectroscopic characterization would be desirable to confirm the existence of the superspheres in solution. A promising approach for this is based on increasing the steric demand on the  $\text{Cp}^R$  ligand by introducing a third *tert*-butyl group on the  $\text{Cp}^R$  ring. For this reason,  $[\text{Cp}''\text{Ta}(\text{CO})_2(\eta^4\text{-P}_4)]$  (**1b**) was synthesized in analogy to the preparation of **1a**<sup>[4]</sup> in good yields (73%). The comprehensive characterization of **1b** in solution as well as in the solid state by X-ray crystallography showed almost identical structural features to those of **1a**.<sup>[13]</sup>

The reactivity of **1b** towards  $\text{CuX}$  ( $\text{X}=\text{Cl}, \text{Br}$ ) was investigated by adding a solution of  $\text{CuX}$  in  $\text{CH}_3\text{CN}$  to a solution of **1b** in toluene or benzene and stirring it for ten minutes. Subsequently, the red solution was layered with  $\text{Et}_2\text{O}$ , and after three weeks, red prisms of **2c** and **2d** had formed (Figure 2). These products were also formed when **1b**/ $\text{CuX}$  ratios ranging from 1:1 to 1:2 were used.

Both **2c** and **2d** crystallized in the monoclinic space group  $P2_1/n$ , and X-ray structural analysis revealed the supramolecules  $[\{\text{Cp}''\text{Ta}(\text{CO})_2(\eta^4\text{-P}_4)\}_6\{\text{CuX}\}_{8-x}]$  (**2c**:  $\text{X}=\text{Cl}$ ,  $x=0.6$ ; **2d**:  $\text{X}=\text{Br}$ ,  $x=0.3$ ; Figure 3a). The molecular structures of **2a–2d** are similar; with the exception of the additional *tert*-butyl group, they exhibit the same spherical supramolecules and alternating patterns of four- and six-membered rings in the 32-vertex core (Figure 3e). The  $O_h$  symmetry of the inorganic scaffold is violated by the organic substituents at the Ta atoms, which leads to overall  $C_{3i}$  (**2b**) or  $C_i$  symmetry (**2c**, **2d**) for the supramolecules in the solid state. The P–P bonds of 2.144(3)–2.176(3) Å in **2d** are only slightly shorter than those in the free complex **1b**<sup>[4]</sup> and supramolecule **2a** (2.156(2)–2.180(2) Å).<sup>[5]</sup> The inner cavities of **2c** and **2d** have the same size ( $d_{\text{inner}}=0.6$  nm) whereas the maximum outer diameters of 2.50 nm (**2c**) and 2.54 nm (**2d**) are larger by about 0.35 nm than those of the  $\text{Cp}''$  derivatives **2a** and **2b**,<sup>[5]</sup> which is due to the third *t*Bu group in the  $\text{Cp}''$  ligands.

Attention needs to be drawn to the co-existence of the supramolecules **2b–2d** with isomeric and slightly incomplete

inorganic scaffolds in the solid state. One CuX unit is missing in the 32-vertex scaffold for 20–50% of the supramolecules. In 10% of the spheres, an additional CuX unit is present, which points into the cavity. In this case, the Cu ion is coordinated to two *cyclo*-P<sub>4</sub> units in η<sup>2</sup>-mode while the terminal X ion is located at the center of the cavity. This CuX unit can either co-exist with adjacent Cu ions σ-coordinated to the *cyclo*-P<sub>4</sub> unit or neighbor a CuX vacancy in the 32-vertex scaffold.<sup>[13]</sup> It thereby forms two or one Cu⋯Cu contacts of 2.81–2.95 Å.

Apparently, the single *t*Bu group also supports the formation of the spherical clusters. However, it induces the formation of even more isomeric forms in addition to the structural variation in the inorganic core. In the free complex **1b**, the Cp<sup>'''</sup> ligands can rotate freely. However, upon coordination to the copper halide units, the rotation is hindered as the halides are now situated in between the *t*Bu groups. With increasing halide size, this immobilization becomes more pronounced. As a consequence, every molecule of complex **1b** can appear in two enantiomeric conformations that differ in the orientation of the single *t*Bu group, which again leads to isomeric clusters. In the crystal structure of **2c**, only one isomer is observed. However, the crystal structure of **2d** consists of co-crystallized epimeric clusters as indicated by the disorder of one *t*Bu group.<sup>[13]</sup> As the formation of the spherical clusters in solution should not be influenced by the orientation of the single *t*Bu group, a freshly prepared solution of **2c** and **2d** should contain several isomeric clusters, which might inhibit the crystallization of the macromolecules. This specific property is in accordance with the experimental observation that even from concentrated mixtures of **1b** with CuX (X = Cl, Br), single crystals of **2c** and **2d** were formed only within several weeks, whereas **2a** and **2b** crystallized within one day.

Compounds **2c** and **2d** are orange, air-sensitive solids, and are insoluble in hexane and Et<sub>2</sub>O. As anticipated, they are sparingly soluble in toluene and have moderate solubility in CH<sub>2</sub>Cl<sub>2</sub>. In the <sup>1</sup>H NMR spectra of **2c** and **2d** in CD<sub>2</sub>Cl<sub>2</sub>, six broad resonances appear between 1 and 2 ppm for the *t*Bu groups and two broad resonances at 6.4 and 7.4 ppm for the methine H atoms. The presence of two resonances for the methine protons indicates the inhibited rotation of the Cp<sup>'''</sup> ligand. The distinct downfield shift of the resonance at 7.4 ppm was attributed to the proximity of the halide ligand. The presence of several broad resonances for the *t*Bu groups is in accordance with the slow isomerization of the clusters in solution. In the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, very broad resonances were observed between –50 and –90 ppm, which were shifted upfield by approximately 100 ppm compared to the free complex **1b**. This indicates that the P<sub>4</sub> cycle interacts with the Lewis acidic copper(I) halides. Furthermore, resonances of the free complex **1b** could be detected neither in the <sup>1</sup>H nor in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. The same observations were made in NMR spectroscopic investigations of a freshly prepared reaction mixture of **1b** and CuX (X = Cl, Br). These results indicate that the spherical aggregates, such as **2c** and **2d**, are formed immediately and remain intact in solution. This hypothesis was also confirmed by diffusion ordered spectroscopy (DOSY) experiments. The hydrodynamic radii

thus determined correlate well with the radii derived from the crystal structure analysis in the solid state.<sup>[13]</sup>

In the ESI mass spectra of **2c** and **2d**, only fragments of the clusters were detected. In CH<sub>2</sub>Cl<sub>2</sub> solutions, the cation [(Cp<sup>'''</sup>Ta(CO)<sub>2</sub>P<sub>4</sub>)<sub>2</sub>Cu]<sup>+</sup> was observed. In CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN mixtures, larger cluster fragments up to [(Cp<sup>'''</sup>Ta(CO)<sub>2</sub>P<sub>4</sub>)<sub>3</sub>Cu<sub>2</sub>Cl]<sup>+</sup> could be detected. The IR spectra show two CO stretching vibrations (**2c**: 2019 cm<sup>-1</sup>, 1979 cm<sup>-1</sup>; **2d**: 2015 cm<sup>-1</sup>, 1973 cm<sup>-1</sup>), which are located at significantly higher wavenumbers than those of **1b** (1982 cm<sup>-1</sup>, 1939 cm<sup>-1</sup>); similar observations were made for the analogous Cp<sup>''</sup> clusters **2a** and **2b**.

Upon addition of a solution of CuI in CH<sub>3</sub>CN to a stirred solution of **1b** in CH<sub>2</sub>Cl<sub>2</sub>, an orange solution was obtained. After stirring the mixture for 4 hours, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the reaction mixture displayed no resonances corresponding to **1b**, but very broad resonances appeared between –30 and –90 ppm, just like in the spectra of the CuCl/Br clusters **2c** and **2d**. However, the corresponding DOSY NMR experiment indicated that the spheres formed in solution have a smaller radius than derivatives **2c** and **2d**.<sup>[13]</sup> In the ESI mass spectrum of the reaction mixture, the cation [(Cp<sup>'''</sup>Ta(CO)<sub>2</sub>P<sub>4</sub>)<sub>2</sub>Cu<sub>2</sub>I]<sup>+</sup> represents the largest fragment, as found for isolated **2c**. After removal of the solvent, two carbonyl bands (2013 cm<sup>-1</sup>, 1971 cm<sup>-1</sup>) appear in the IR spectrum of the obtained solid, which are similar to those of the clusters **2c** (2019 cm<sup>-1</sup>, 1979 cm<sup>-1</sup>) and **2d** (2015 cm<sup>-1</sup>, 1973 cm<sup>-1</sup>), but also correspond to those of **3** (2011 cm<sup>-1</sup>, 1969 cm<sup>-1</sup>) and **4** (2017 cm<sup>-1</sup>, 1976 cm<sup>-1</sup>). Both the solubility of these species and the analytical data indicate the presence of spherical aggregates in solution with structures similar to, but smaller than, those of the clusters **2c** and **2d**. Incomplete spheres thus seem to exist in solution that might be structurally comparable to fragments of **4** after CuI release or sections of **3**. However, upon layering diethyl ether over the reaction mixture, yellow plates of the 2D polymer **5** were formed (Figure 2d), which were insoluble in hexane, Et<sub>2</sub>O, toluene, CH<sub>2</sub>Cl<sub>2</sub>, and THF.

X-ray structure analysis of **5** revealed the 2D coordination polymer [Cp<sup>'''</sup>Ta(CO)<sub>2</sub>(η<sup>4</sup>-P<sub>4</sub>){Cu<sub>4</sub>(μ<sub>3</sub>-I)<sub>4</sub>}]<sub>n</sub>, in which *cyclo*-P<sub>4</sub> ligand complexes **1b** link {Cu<sub>4</sub>(μ<sub>3</sub>-I)<sub>4</sub>} heterocubane units in a 1,2,3,4-coordination mode (Figure 3h). Even though these complexes **1b** feature the same coordination mode as in the spherical molecules **2c** and **2d**, the Cu<sub>4</sub>I<sub>4</sub> units induce the formation of the layered structure in **5**. Therefore, every second complex **1b** is located on the opposite side of the polymeric layer.<sup>[13]</sup> Compared with the free complex **1b**, the average P–P bond is also shorter in **5** (2.150(6) Å). The Cu<sub>4</sub>I<sub>4</sub> heterocubane structural motif is known in coordination chemistry.<sup>[11]</sup> In **5**, each iodine atom bridges three copper atoms with an average Cu–I distance of 2.66(4) Å, which lies in the typical range for such bonds.<sup>[12]</sup> The resulting layers of Cu<sub>4</sub>I<sub>4</sub> and *cyclo*-P<sub>4</sub> units are separated by the bulky Cp<sup>'''</sup> ligands and the carbonyl ligands at the Ta atoms as well as co-crystallized CH<sub>3</sub>CN solvent molecules.

In summary, a systematic study towards spherical supramolecules starting from the *cyclo*-P<sub>4</sub>-containing tantalum complexes **1a** and **1b** as building blocks has yielded fascinating supramolecular assemblies with a non-classical fullerene

topology. The CuX-based superspheres (X = Cl, Br; **2b–d**) thus obtained mostly exhibit hollow 32-vertex scaffolds in the shape of a truncated octahedron that exclusively consists of alternating P<sub>4</sub> four- and Cu<sub>2</sub>P<sub>4</sub> six-membered rings. In the solid state, isomeric and slightly incomplete supramolecules with lower symmetry were also observed. The higher steric demand in Cp<sup>'''</sup> derivative **1b** compared to **1a** improved the solubility of these 2.5 nm large molecules. NMR spectroscopic studies confirmed that **1b**-based spherical aggregates are immediately assembled and remain intact in solution. Although **1b** did not give rise to molecular clusters in the reaction with CuI, **1a** enabled the synthesis of the previously unknown supramolecules **3** and **4** with sizes of up to 2.2–2.8 nm. Cluster **3** consists of two open shells similar to those in **2** that are fused together by two Cu<sub>3</sub>I<sub>3</sub> units to give an unprecedented peanut-shaped scaffold of 58 non-carbon atoms. The 41-vertex supramolecule **4** exhibits a completely new topology. A hemisphere of five *cyclo*-P<sub>4</sub> and four [Cu<sub>2</sub>I]<sup>+</sup> units closed by a Cu<sub>4</sub>I<sub>5</sub><sup>-</sup> bowl results in a pear-shaped inorganic framework, where, in contrast to **3**, the iodides are also involved in scaffold construction. However, both structures can be viewed as snapshots of the formation of the 32-vertex balls as the missing TaP<sub>4</sub> unit of the 32-vertex ball can be replaced by a CuI network to form **4** or merged to a second incomplete ball via a (CuI)<sub>x</sub> moiety to form peanut-shaped compound **3**.

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- [1] a) A. Popov, S. Yang, L. Dunsch, *Chem. Rev.* **2013**, *113*, 5989–6113; b) D. Jariwala, V. K. Sangwan, L. J. Lauhon, T. J. Marks, M. C. Hersam, *Chem. Soc. Rev.* **2013**, *42*, 2824–2860; c) C.-Z. Li, H.-L. Yip, A. K. Y. Jen, *J. Mater. Chem.* **2012**, *22*, 4161–4177; d) F. D'Souza, O. Ito, *Chem. Soc. Rev.* **2012**, *41*, 86–96; e) R. W. Sallfrank, A. Scheurer, *Top. Curr. Chem.* **2012**, *314*, 125–170; f) M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, New York,

- 1996**; g) P. W. Fowler, D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon, Oxford, **1995**; h) H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162–163.
- [2] a) A. Schindler, C. Heindl, G. Balazs, C. Groeger, A. V. Virovets, E. V. Peresyphkina, M. Scheer, *Chem. Eur. J.* **2012**, *18*, 829–835; b) M. Scheer, A. Schindler, C. Gröger, A. V. Virovets, E. V. Peresyphkina, *Angew. Chem. Int. Ed.* **2009**, *48*, 5046–5049; *Angew. Chem.* **2009**, *121*, 5148–5151; c) J. Bai, A. V. Virovets, M. Scheer, *Science* **2003**, *300*, 781–783; d) F. Dielmann, M. Fleischmann, C. Heindl, E. V. Peresyphkina, A. V. Virovets, R. M. Gschwind, M. Scheer, *Chem. Eur. J.* **2015**, *21*, 6208–6214; e) E. V. Peresyphkina, C. Heindl, A. Schindler, M. Bodensteiner, A. V. Virovets, M. Scheer, *Z. Kristallogr. Cryst. Mater.* **2014**, *229*, 735–740; f) S. Heindl, E. Peresyphkina, J. Sutter, M. Scheer, *Angew. Chem. Int. Ed.* **2015**, *54*, 13431–13435; *Angew. Chem.* **2015**, *127*, 13631–13635.
- [3] a) R. L. Murry, D. L. Strout, G. K. Odom, G. E. Scuseria, *Nature* **1993**, *366*, 665–667; b) Bharat, R. Bhola, T. Bally, A. Valente, M. K. Cyranski, L. Dobrzycki, S. M. Spain, P. Rempala, M. R. Chin, B. T. King, *Angew. Chem. Int. Ed.* **2010**, *49*, 399–402; *Angew. Chem.* **2010**, *122*, 409–412; c) W. Qian, S.-C. Chuang, R. B. Amador, T. Jarrosson, M. Sander, S. Pieniazek, S. I. Khan, Y. Rubin, *J. Am. Chem. Soc.* **2003**, *125*, 2066–2067.
- [4] O. J. Scherer, R. Winter, G. Wolmershäuser, *Z. Anorg. Allg. Chem.* **1993**, *619*, 827–835.
- [5] B. P. Johnson, F. Dielmann, G. Balazs, M. Sierka, M. Scheer, *Angew. Chem. Int. Ed.* **2006**, *45*, 2473–2475; *Angew. Chem.* **2006**, *118*, 2533–2536.
- [6] a) Y. D. Gao, W. C. Herndon, *J. Am. Chem. Soc.* **1993**, *115*, 8459–8460; b) H. W. Kroto, *Nature* **1987**, *329*, 529–531.
- [7] C. Heindl, E. V. Peresyphkina, A. V. Virovets, W. Kremer, M. Scheer, *J. Am. Chem. Soc.* **2015**, *137*, 10938–10941.
- [8] The diameters *d* of the inner cavities were calculated as the minimum distances between geometrically opposed atoms minus the van der Waals radii of the respective atoms (P: 0.180 nm, Cu: 0.140 nm, I: 0.198 nm). The *d* value was defined as the diameter of the largest sphere that can be inscribed in the cavity formed by the atoms. The outer diameter was taken as the maximum distance between two atoms the most distant from the center, plus twice the van der Waals radius for the H atom (0.12 nm).
- [9] a) C. Schwarzmaier, A. Schindler, C. Heindl, S. Scheuermayer, E. V. Peresyphkina, A. V. Virovets, M. Neumeier, R. Gschwind, M. Scheer, *Angew. Chem. Int. Ed.* **2013**, *52*, 10896–10899; *Angew. Chem.* **2013**, *125*, 11097–11100; b) F. Dielmann, A. Schindler, S. Scheuermayer, J. Bai, R. Merkle, M. Zabel, A. V. Virovets, E. V. Peresyphkina, G. Brunklaus, H. Eckert, M. Scheer, *Chem. Eur. J.* **2012**, *18*, 1168–1179.
- [10] J. Bai, A. V. Virovets, M. Scheer, *Angew. Chem. Int. Ed.* **2002**, *41*, 1737–1740; *Angew. Chem.* **2002**, *114*, 1808–1811.
- [11] R. Peng, M. Li, D. Li, *Coord. Chem. Rev.* **2010**, *254*, 1–18.
- [12] A. Vega, J.-Y. Saillard, *Inorg. Chem.* **2004**, *43*, 4012–4018.
- [13] See the Supporting Information.

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