Influence of the Substitution Pattern of Cp-Iron-Arene Salts in the Solid-State Synthesis of New Carbon Nanostructures

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A series of Cp-iron-arene hexafluorophosphate salts have been prepared and pyrolyzed under autogenous pressure. It was found that the resulting carbon nanostructures were highly dependent on the starting material. Even a small change in the substitution pattern of the arene ligand could result in different material. In addition to very short hollow carbon nanofibers, also called carbon nanocapsules, it was possible to prepare long homogeneous carbon fibers in quantitative yield, which incorporated iron phosphorus composite particles in remarkable continuous distances.

1. Introduction

In addition to single-walled and multiwalled carbon nanotubes,[1–4] various more or less related structures, including carbon nanohorns,[5–7] carbon nanospheres,[8–11] and onion-like carbon structures.[12,13] have been prepared. If these structures contain metals, they have additional potential as magnetic particles, contrast agents, protecting cloaks, and catalysts, and in other applications.[4,14–18] Despite their emerging applications such structures in addition to carbon nanotubes are often relatively difficult to produce in bulk compared to carbon nanotubes. Occasionally, they were produced only as byproducts during the preparation of carbon nanotubes.[10,19,20] Arc-discharge using metal-doped graphite rods,[6,21] pyrolysis of carbonizing mixtures,[22–24] or catalytically assisted chemical vapor deposition (CCVD) methods are some of the involved methods.[25–28] For example, the group of C. N. R. Rao reported first some CVD processes involving the pyrolysis of ferrocene in an open system with a flow of argon with or without a hydrocarbon source, which leads to carbon nanotubes.[29–31] Several of these procedures require relatively complex setups and can have limitations over the range of metals and the amount of filling. Another option to prepare these structures is the pyrolysis of different organometallic complexes in a sealed vessel under autogenous pressure, which can lead to carbon nanotubes,[32–35] carbon nanocables,[34,36] onions,[34,37] and microspheres.[35]

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Figure 1. Cp(Fe)arene salts.

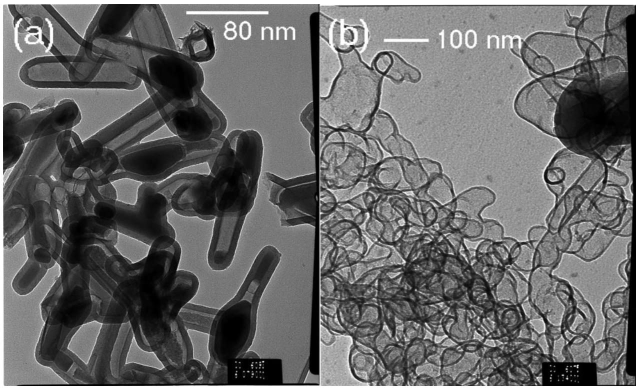
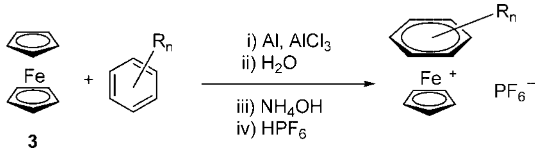


Figure 2. (a) TEM image of material from pyrolyzed complex **1** and (b) TEM image of material from pyrolyzed complex **2**.

Scheme 1. Preparation of Cp(Fe)arene Salts from Ferrocene[39,42]

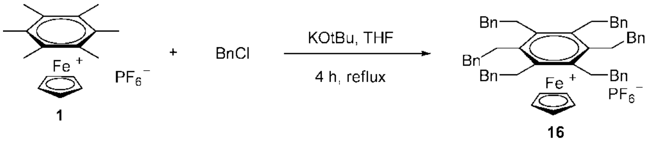


Recently, we found a straightforward method to prepare a novel nanocarbon structure, carbon nanocapsules filled with Fe−P composite, in near quantitative yield (Figure 2a).[38] The new particles were obtained via the simple pyrolysis of CpFe(arene) salt **1**[39] at 700 °C under autogenous pressure in a sealed vessel and can be described as short hollow carbon fibers.

In addition complex **2**[40] resulted in some form of coral carbon structure, whose picture is shown in Figure 2b.

Here an investigation on the influence of different substitution patterns of the starting complexes on the resulting material and functionalization studies of the obtained material will be presented.

Scheme 2. Preparation of Salt 16[43]



2. Results and Discussion

In addition to complexes **1**[39] and **2**[40] complexes **4**−**13**[39] and **14**[41] were prepared according to the literature as shown in Scheme 1. Starting with ferrocene, one Cp ligand can be simply exchanged with the desired arene in the presence of aluminum, aluminum chloride, and equimolar amounts of water at 100 °C after several hours. The desired salts were precipitated after workup by the addition of HPF_6. The salts chosen for this investigation are depicted in Figure 3.

In addition complex **16** was prepared according to Scheme 2 by the reported procedure of Astruc et al. by treating complex **1** with benzyl chloride in the presence of a strong base in THF under reflux.[43]

The complexes were then pyrolyzed under the same conditions reported for complex **1** for 2 h at 700 °C in an evacuated sealed quartz tube. Some of the resulting pyrolyzed material, which is similar to the observed nanocapsules from salt **1**, is depicted in Figure 4. However in the beginning ferrocene **3** was pyrolyzed at 700 °C, which resulted in the same observation recently reported by Coville et al.[35] Amorphous carbon in addition to some MWCNTs was obtained as the major product. This shows the considerable difference of this method compared to CVD processes, where ferrocene has been successfully used for the synthesis of MWCNTs.[28–31] The comparison of the two methods for the presented salts is not possible since these compounds cannot be sublimed. Only decomposition is observed, which makes them ideal for application in solid-state pyrolysis.

It is possible to see in Figure 4 that five analogues of salt **1** resulted in similar structures during the pyrolysis at 700 °C. The benzene analogue **4** also gave nanocapsules; however they were not completely developed and not separated from each other (Figure 4a). This material resembles some recently prepared nanocages by Holmes et al.[44] The cages were synthesized by the deposition of *p*-xylene over a Mo/Co catalyst in supercritical carbon dioxide. The toluene analogue **5** resulted in a few half-developed capsules (Figure 4b). The 1,2,3-trimethylbenzene salt **10** showed nearly the same result as salt

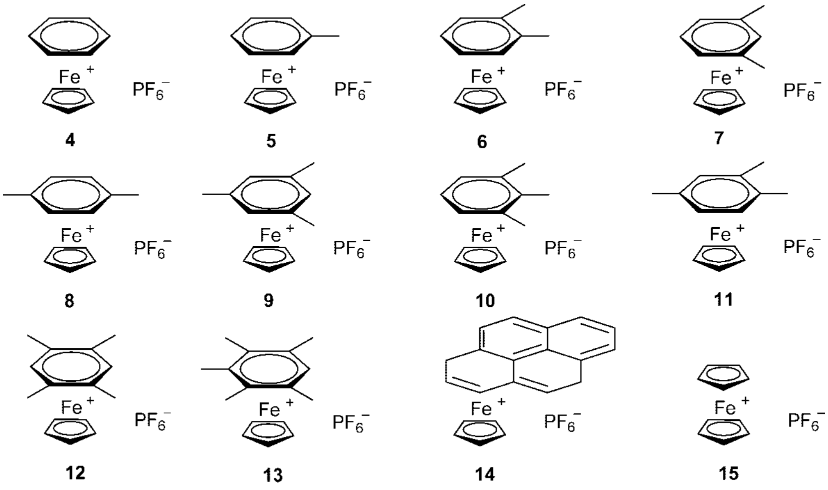


Figure 3. Salts prepared according to Scheme 1 (**1**−**14**) and purchased salt **15**.

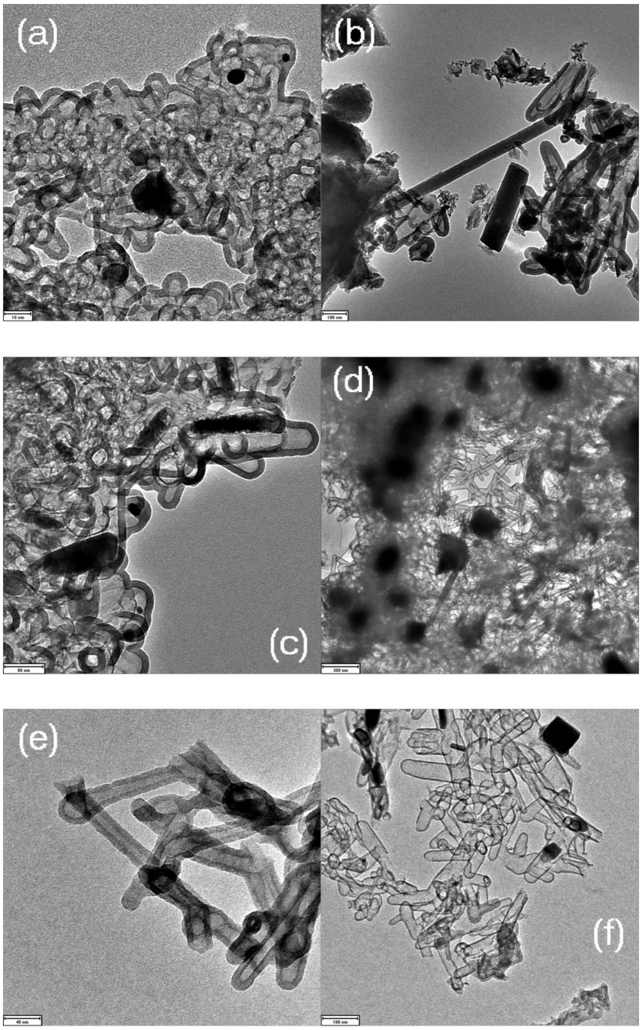


Figure 4. TEM images of pyrolyzed material at 700 °C for 2 h from (a) complex **4**, (b) complex **5**, (c) complex **10**, (d and e) complex **12**, and (f) complex **13**.

5 (Figure 4c), while the 1,2,4,5-tetramethylbenzene complex **12** gave nanocapsules in good yield as obtained by hexamethylbenzene complex **1** (Figure 4d,e). However, a small amount of amorphous carbon was present and the quality of the capsules was slightly lower compared to those from salt **1**. Finally the pentamethylbenzene salt **13** resulted in capsules that had a far smaller wall thickness compared to complex **1** (Figure 4f).

Although very similar to the complexes presented so far, the 1,2-dimethylbenzene salt **6** and its 1,3- and 1,4-analogues **7** and **8** gave only amorphous carbon as the major product when pyrolyzed at 700 °C. Similar results were found by the pyrolysis of the 1,2,4-trimethylbenzene salt **11**. Additionally, the arene complexes were also pyrolyzed at 500 °C for 2 h. All arene salts gave mainly amorphous carbon, except complexes **1** and **13**, which resulted in nanocapsules, however with low quality.

A remarkable exception is the 1,3,5-trimethylbenzene complex **9**. Pyrolysis of this complex at 500 °C resulted in less developed nanocapsules, as shown in Figure 5a. However, when the salt was pyrolyzed at 700 °C, carbon fibers in nearly quantitative yield were obtained (Figure 5b,c,d). These fibers (for HRTEM see the Supporting Information) had a diameter between 35 and 280 nm with a length varying between 3.2 and 10 μm. Nearly all of the fibers, like the nanocapsules in our previous study,[38] had Fe−P nanoparticles incorporated, which were analyzed by EDX (see the Supporting Information). Remarkable is the regular spacing of the particles. The distance between two particles inside a fiber is nearly always double the diameter of the fiber. In most of cases the diameter of a particle was found to be 80% of the diameter of the fibers; however sometimes a few particles were found having a diameter larger than the fiber they were incorporated in. One should point out at this stage the dramatic effect that the difference of the starting material has comparing for example the results obtained from the 1,3,5-trimethylbenzene salt **9** and the 1,2,3-trimethylbenzene salt **10**.

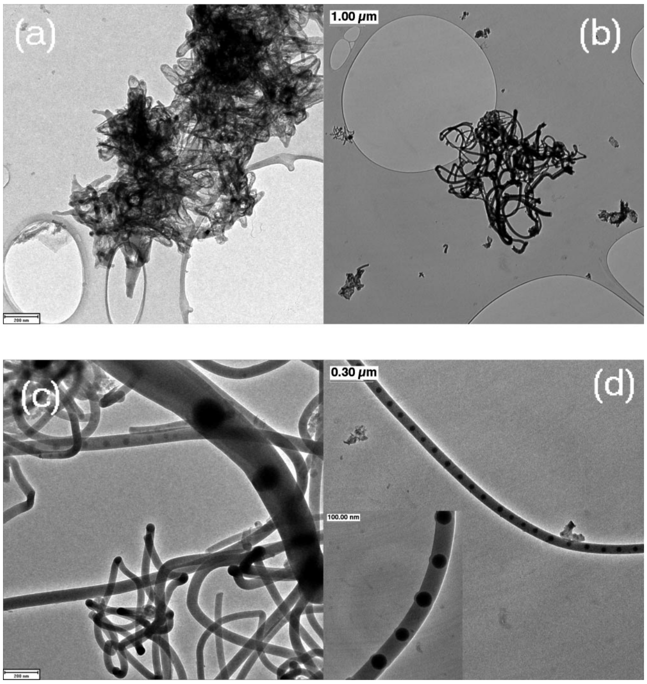


Figure 5. TEM images of pyrolyzed material of complex **9** (a) at 500 °C and (b, c, and d) at 700 °C.

Some of the above-described complexes, which gave mainly amorphous carbon in the pyrolysis experiments, showed some other well-defined nanostructures, although in a low yield between 5% and 10% estimated from TEM analysis, and are presented in Figure 6.

Complex **15** resulted at 700 °C in a small amount of carbon microspheres (Figure 6a) with a diameter up to 800 nm. Complex **16** resulted at 500 °C in microspheres with a diameter of up to 1200 nm (Figure 6b). With complex **5** at 500 °C some well-defined microhorns were found with a length between 4300 and 5300 nm and a diameter of 540 nm. The walls were 75 nm thick (Figure 6c). The pyrolysis of salt **11** at 500 °C also led to microhorns with an average length of 3700 nm and a diameter of 520 nm. The walls were 32 nm thick (Figure 6d−f). On the surface some Fe−P nanoparticles can be observed, which was confirmed by EDX (see the Supporting Information). In addition when complex **16** was pyrolyzed, some nanodonuts were detected (Figure 6f). This form has been recently found in material from asteroids.[45]

In order to evaluate if phosphor is necessary for obtaining nanostructured material, complex **1** with a BF_4 counteranion[39] was prepared and pyrolyzed at 700 °C for 2 h. Although no well-defined nanocapsules were observed, some coral-like nanostructure was found (see Figure 7). This indicates that the anion has an influence on the resulting material.

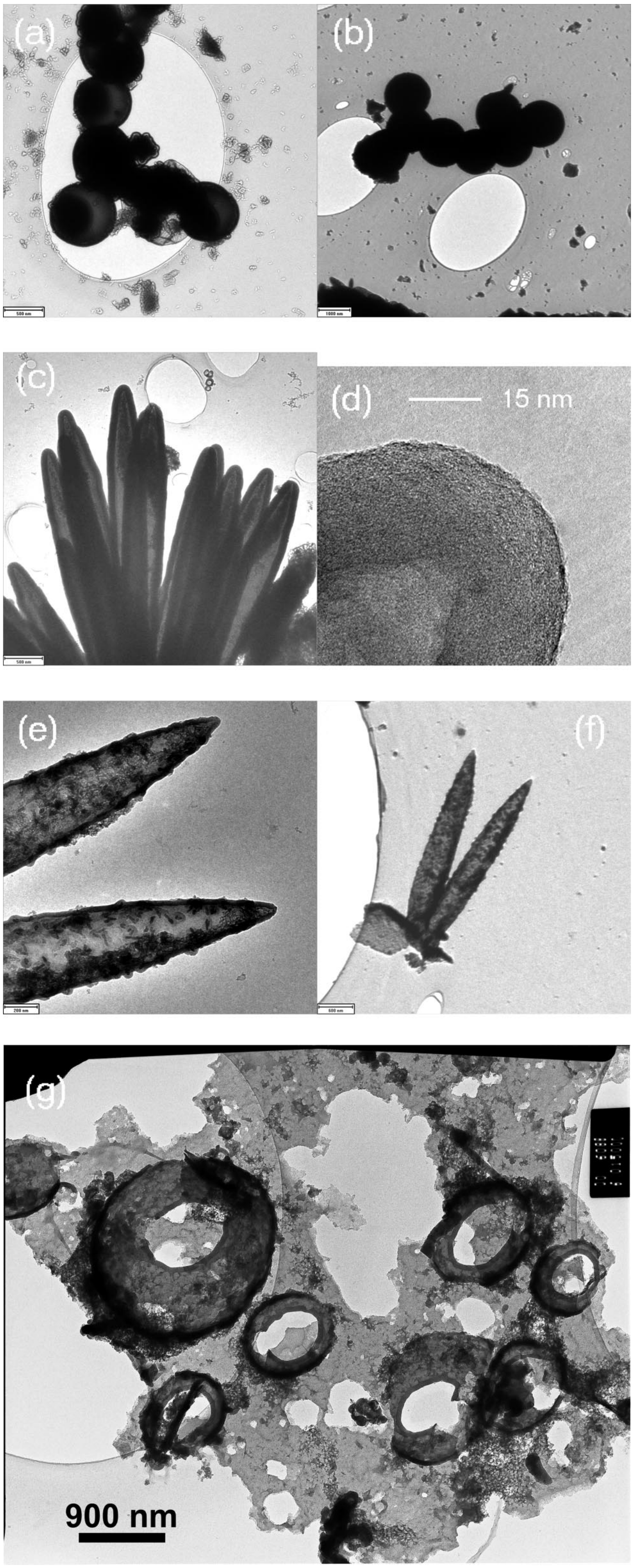


Figure 6. TEM images of pyrolyzed material of (a) complex **15** at 700 °C, (b) complex **16** at 500 °C, (b, c) complex **5** at 500 °C, (d, e, and f) complex **11** at 500 °C, and (g) complex **16** at 900 °C.

3. Conclusions

It was possible to show that novel carbon nanostructures are accessible via the pyrolysis of Cp-Fe-arene hexafluorophosphate salts. In the case of complexes **1** and **9** the material was obtained in nearly quantitative yield. In addition several new well-defined carbon nanostructures were found. It was also shown that even the smallest change in the substitution pattern in the starting arene salt had a dramatic effect on the result. Nanocapsule-related material was obtained from complexes **4**, **5**, **10**, **12**, and **13** at 700 °C after 2 h and complex **9** at 500 °C. Long nanofibers were obtained from complex **9** at 700 °C after 2 h, and short tubular structures were prepared from complex **5**. Spherical structures were found with complex **15** at 700 °C and complex **16** at 500 and 900 °C. In all samples no fluoride was observed, which can be explained by the use of sealed quartz tubes. Clearly the fluoride must have reacted with this material. However, to predict a resulting nanostructure from a certain starting material and to understand the mechanism of the pyrolysis remain difficult, and as shown, no obvious trend can be observed. The presented nanostructured material could have, for example, high potential for gas-storage media,[46,47] Li-intercalation materials for batteries,[48] and cold electron field emitters.[49]

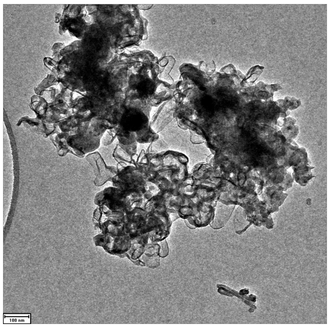


Figure 7. TEM images of pyrolyzed material of complex **1** with a BF_4 counteranion.

4. Experimental Section

Salts **1**,[39] **2**,[40] **3**−**13**,[39] and **14**[41] were prepared according to a literature procedure.[42] Salt **1** with BF_4 as a counteranion was prepared according to the literature.[39] Salt **15** was purchased from Aldrich. Salt **16** was prepared according to the literature.[43] Pyrolytic combustion experiments were performed in an alumina work tube placed horizontally in a Carbolite furnace. General morphology of the samples obtained was observed with a Philips CM200 FEG (operated at 120 kV) and a Philips CM 400 (operated at 200 kV) transmission electron microscope equipped with an energy-dispersive X-ray spectrometer (EDS). Samples for TEM were prepared by dispersing the material in 2-propanol and then placing it onto a copper grid coated with a holey carbon film.

For the pyrolysis, complexes were sealed under vacuum in a quartz tube. The latter was placed in a furnace and heated at a rate

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of 10 °C/min to 500, 700, or 900 °C. It was then kept at that temperature for 2 h and left to cool to rt. The sealed tube was opened, and no internal pressure was found. The soot was collected and stirred in concentrated HCl for 15 h and was further washed several times with deionized water. The sample so obtained was dried in an oven at 60 °C overnight.

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Supporting Information Available: This material with EDX scans and additional TEM images is available free of charge via the Internet at http://pubs.acs.org.

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