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Synthesis and Explosive Decomposition of Organometallic Dehydro[18]annulenes: An Access to Carbon Nanostructures

Matthew Laskoski, Winfried Steffen, Jason G. M. Morton, Mark D. Smith, and
Uwe H. F. Bunz*

*Contribution from the USC NanoCenter and the Department of Chemistry and Biochemistry,
The University of South Carolina, Columbia, South Carolina 29208*

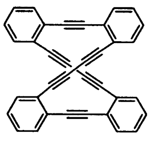
Received May 6, 2002

Abstract: The synthesis of eight new cyclobutadiene or ferrocene-fused organometallic dehydroannulenes is reported. Cadiot-type coupling of a 1-bromoethynyl-2-silylethynylbenzene derivative to an organometallic diyne (1,2-diethynyl-3,4-bis(trimethylsilyl)cyclobutadiene(cyclopentadienyl)cobalt or 1,2-diethynylferrocene) is followed by deprotection and $Cu(OAc)_2$-promoted ring closure. Five of the organometallic dehydroannulenes were structurally characterized. Three of the novel cycles explode at temperatures from 196 to 293 °C and form insoluble carbon materials. The soot produced from **13a** shows a high abundance of onion-like carbon nanostructures. The nanostructures were characterized by high-resolution transmission electron microscopy.

Introduction

We describe the synthesis, structural characterization, and explosive decomposition of organometallic dehydro[18]annulenes containing ferrocene or cyclobutadiene(cyclopentadienyl)cobalt units. The explosive decomposition of the dehydroannulene **13a** gives rise to the formation of onion-type carbon nanostructures.

Since the beginning of the nineties, the chemistry of "unnatural" carbon allotropes has flourished. Fullerenes, carbon onions, nanotubes, and all-carbon ropes are of great interest as hydrogen storage containers, cloaking layers, and catalysts.[1−5] Nanotubes have been made mostly by pyrolytic and high-energy ablation routes of small molecules or arc evaporation of solid graphite. The conversion of small molecules into carbon nanomaterials is promoted by transition-metal catalysts.[6] However, high temperatures and suitable equipment are necessary for these experiments. Examples of all-carbon molecules from polyynes are Rubin's[7a] and Tobe's[7b] access to C_{60}[8] by pyrolysis of cyclophane precursors.



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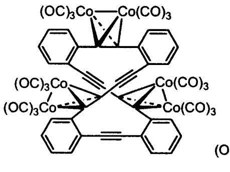

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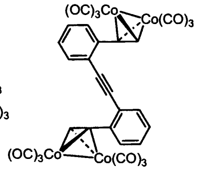

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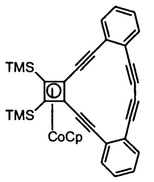

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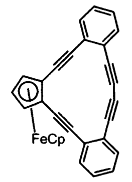

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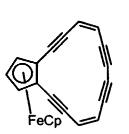

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Oligoynes and polyynes are known to explosively decompose upon heating or rubbing.[9,10] Vollhardt demonstrated elegantly that the products of these reactions can be closed-shell carbon structures, such as carbon onions or metal-filled carbon nanotubes.[10] The authors examined different exploding oligoynes and found that structures **1−3** gave closed-shell carbon materials. They contended that the explosion of carbon-rich materials may be a general way to make carbon nanostructures. From our experience and the lack of other literature references, it seems

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* Address correspondence to this author. E-mail: Bunz@mail.chem.sc.edu.

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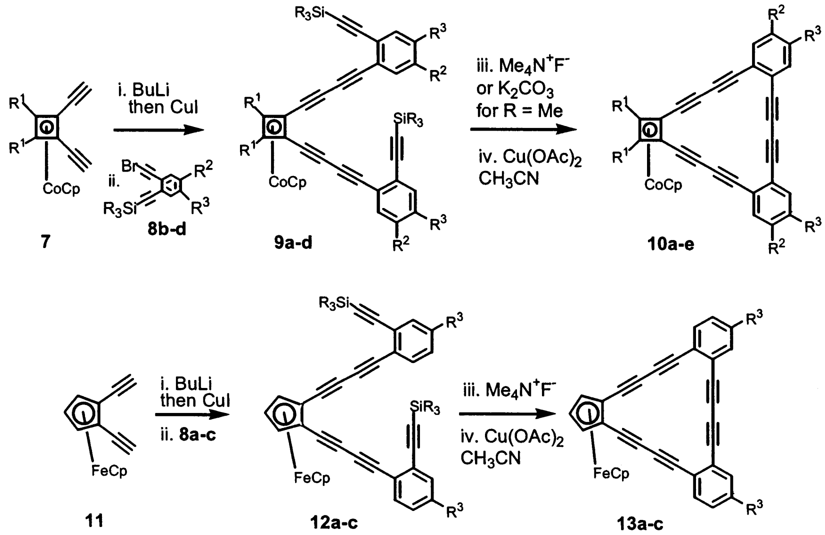
Scheme 1 [a]



[a] The synthesis of **9a** uses a slightly different route, not via **8a.** See Supporting Information for details.

Table 1. Substituent Key for **7-10** and Yields for **9-10**

	R for 8^a,9	R^1 for 7, 9, 10	R^2	R^3	yield **9**	yield **10**	overall yield
a	methyl^a	SiMe$_3$	H	H	40%	9%^{b}	4%^{b}
b	isopropyl	**7**, **9**, R^1 = SiMe$_3$; **10b**, R^1=H	H	isopropyl	35%	57%	20%
c	isopropyl	SiMe$_3$	H	*tert*-butyl	73%	13%^{c}	9%
d	isopropyl	SiMe$_3$	butyl	butyl	57%	58%	33%
e		H	H	*tert*-butyl		17%^{c}	12%

[a] For **9a**, the bromoyne **8a** (R = isopropyl) is not utilized. See Supporting Information for a modified procedure. For simplicity, **9a** is included in Table 1. [b] Cycle **10a** is only marginally soluble. [c] Combined yield = 30%. Entries **c** and **e** represent one experiment.

Table 2. Substituent Key and Yields for **12-13**

	R for **8**,**12**	R^3	yield **12**	yield **13**	overall yield
a	isopropyl	H	45%	75%	34%
b	isopropyl	isopropyl	62%	44%	27%
c	isopropyl	*tert*-butyl	56%	57%	32%

Table 3. DSC Data of the Macrocycles **10** and **13**^{a}

compound	temperature (°C)	ΔH_{rxn} (kcal/mol^{-1})
10a	234	−53
10b	202	−153
10c	210, 354	−15, −5
10d	293	−136
10e	243	−93
13a	196	−118
13b	183, 286	−8, −13
13c	190	−144

[a] **10b**, **10d**, and **13a** contain solvent in their crystal lattices. These three are the exploding cycles. The other cycles turn dark and form insoluble materials without explosive decomposition. Vollhardt reported less exothermic reactions (−47 to −53 kcal mol^{-1}) for his exploding alkynes.[10]

though that only very few oligoynes give *defined* carbon nanostructures upon explosion.[10] The organometallic dehydroannulene **13a** is one of them.

Results and Discussion

Our interest in carbon-rich organometallic materials[11] led us to prepare the organometallic dehydroannulenes **4**−**6** to quantify the aromaticity of the cyclopentadienyl rings in ferrocene and the cyclobutadiene rings in cyclobutadiene(cyclopentadienyl)-cobalt.[12] When heated, we found **4**−**6** either to be thermally stable or to polymerize to an amorphous but infusible, insoluble dark material.[13] No explosive decomposition was evidenced.

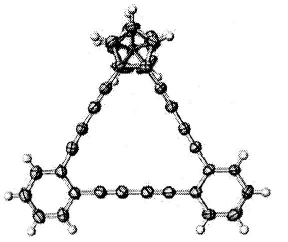


Figure 1. ORTEP representation of the crystal structure of dehydroannulene **13a**.

A larger number of butadiynes per dehydroannulene ring might increase their propensity to explode. An access to nanostructured forms of carbon may result. We anticipated that such explosive transformations could be feasible; Fe, Co, and Ni are known to catalyze nanotube formation,[6] and the projected dehydroannulenes **10** and **13** do contain either Fe or Co.

Syntheses. Vollhardt's diethynylcyclobutadiene complex **7**[14] was metalated with butyllithium and treated with CuI to furnish a cuprate that was coupled to bromo-ynes **8b**−**d** (Scheme 1). This approach is similar to that reported by Rubin,[15] Haley,[16] and Scott.[17] It furnished **9** in yields from 35 to 73% (Table 1).

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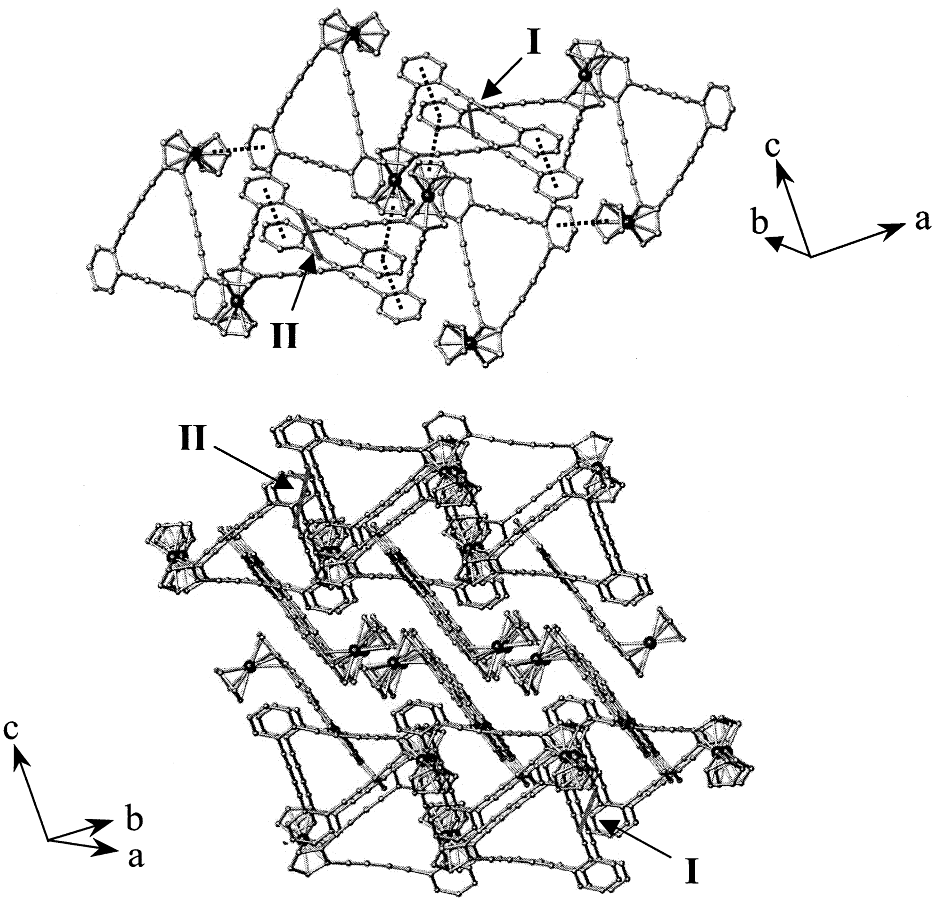

Figure 2. Packing diagram of **13a.** Disordered solvent molecules (dichloromethane and hexanes) are omitted. Crystallographic axes are included for orientation. Top: centroid−centroid (shown with dotted lines) and $C_{alkyne}-C_{alkyne}$ distances are in the range of 3.59 (distance **I**) and 3.68 Å (distance **II**). The interplanar angles between neighboring phenyl rings are close to 7°. Bottom: alternate view of the $\pi-\pi$ stacks (horizontal and into the figure).

The open chain precursors are obtained after desilylation with either $Me_4N^+F^-$ or K_2CO_3 (if R = Me). Crude solutions of the diynes are cyclized in situ by addition of $Cu(OAc)_2$ and acetonitrile. This coupling[18] leads to cycles **10** in yields ranging from 9 to 58%. The low yield of **10a** is due to its marginal solubility that hindered isolation and column chromatography. In the deprotection/cyclization of **9c**, we find the formation of the expected cycle **10c** in a 13% yield. The main product is the dehydroannulene **10e** (17%) that has lost the trimethylsilyl groups off the cyclobutadiene ring under the conditions of the deprotection reaction.

Likewise, **9b** furnishes the desilylated cycle **10b** in 57% yield. The synthetic sequence is applicable to make the ferrocene-based dehydro[18]annulenes **13a**−**c**. Diethynylferrocene **11** is transformed into its cuprate and coupled to **8a**−**c** furnishing **12a**−**c** in yields ranging from 45 to 62% (Table 2). Deprotection and ring closure are performed analogously to the experiments described in the cyclobutadiene series. The dehydroannulenes **13a**−**c** formed in 44−75% yield. This two-step process gave the organometallic dehydro[18]annulenes **10** and **13**, in *overall* yields from 4 to 34%. The copper-promoted ring closure proceeds fairly well, but not as easily[16] as in the dehydro[14]-annulenes **4**−**6**, where yields of up to 93% are realized. The reduced yields may be due to oxidation of the organometallic moieties. The formation of a significant amount of an insoluble and intractable dark material was always observed. Open chain or cyclic dimers or higher oligomers were not detected. It has been reported that alkynylated ferrocenes[19] do not oxidatively dimerize in high yields under the Glaser−Eglinton conditions. The dehydro[18]annulenes can be stored under ambient conditions for days and are indefinitely stable in the freezer. While determining the melting points of **10** and **13,** we noticed that **10b**,**d** and **13a** explode. Ferrocenes **13b**,**c** undergo a solid-state reaction. They turn black and amorphous at 183 and 190 °C, respectively. To quantitate this behavior, we performed DSC analysis of the cycles (Table 3), all of which undergo an exothermic transformation between 183 °C and 293 °C.

Structural Characterization of the Dehydroannulenes. Suitable crystalline specimens of **10b,d,e** and **13a,b** were obtained at room temperature by slow evaporation from a dichloromethane/hexane mixture. Details of the structure determination and the CIF files are given in the Supporting Information.

The molecular geometries of the cycles are similar. The structure of one representative compound, **13a**, is displayed (Figure 1, ORTEP). The dehydro[18]annulene system is structurally undisturbed by the fusion of ferrocene to the perim-

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eter. The bond lengths and bond angles are in agreement with literature values for ferrocenes and dehydrobenzoannulenes.[11,12,16,20] The packing of **13a** in the solid state is displayed in Figure 2. The packing is different from the packing of the other cycles. There are numerous close contacts[13,21] between the diyne units in **13a** (see Figure 2) that are in the range of the sum of the van der Waals radii (3.6 Å) of sp-carbons. Such interactions of the diyne groupings are observed only in the packing of **13a**.

Thermal Decomposition of 10 and 13: Formation of Carbon Nanostructures.[22,23] The exploding cycles were identified from the DSC and melting-point data. All of the exploding cycles contained disordered crystal solvent. The cycles **10b**,**d** and **13a** were subjected to a semipreparative (20−50 mg scale) explosion under vacuum in a Schlenk flask. Despite the large amount of energy released during the explosion, larger quantities (100−200 mg) of the cycles could be exploded in a vacuum-sealed thick-walled quartz tube. Black magnetic powders resulted. The explosion of **10b**,**d** gave amorphous materials with no discerning features on the nanoscale. Only the ferrocene cycle **13a** exploded to form large amounts of distinct carbon nanostructures.[24] According to ^{57}Fe Mössbauer spectroscopy, the soot obtained by the explosion of **13a** contains iron hydroxide, iron oxide, and some elemental iron. Iron carbides were not detected in these samples. Washing and digeration with dilute HCl (2 N) removed the iron-containing contaminants.

Transmission electron microscopy was performed on the HCl-treated soot. Figure 3 shows representative examples of onion-shaped carbon nanostructures. These are obtained from **13a**; the ring-shaped structures are abundant in the soot. Onion structures are visible on all examined grids and on single grids in different places. At low magnification, these onion-shaped materials do not display an internal structure and we initially assumed that the soot was amorphous carbon. However, at higher magnification, the onion-type rings exhibit a layered structure (width 1.8−2.0 nm). Even though layers/tubes can be distinguished, we were not able to see the graphitic spacings that are usually recognizable in carbon onions. A possible reason for the lack of fine structure is the low temperature at which these nanostructures form.

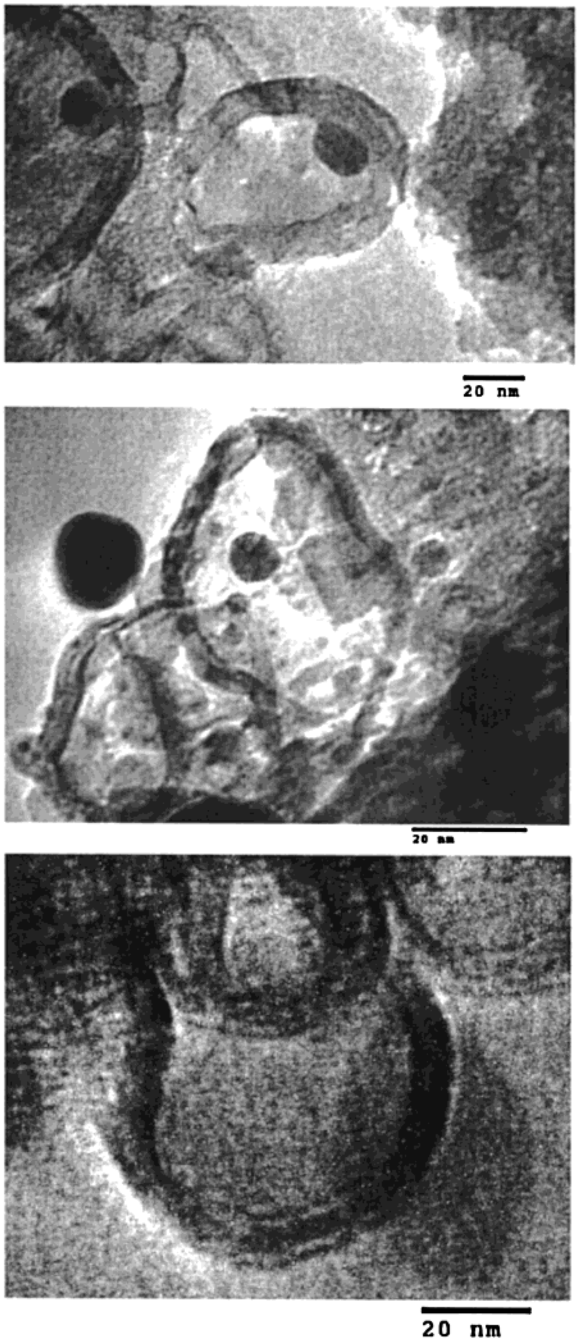

Figure 3. High-resolution transmission electron micrographs of the carbon nanostructures formed by explosion of **13a.** The bottom picture shows the TEM of an annealed sample (to 900 °C).

Upon annealing to 900 °C, we found that the order in the nanostructures increased (Figure 3, bottom). The classification of these structures[22] is not completely clear. Probably, these are carbon onions similar to those described by Ugarte.[22e] Alternatively, they could be multiwalled-bent carbon nanotubes, carbon tori,[1b] or ribbon polymers (Figure 3, middle left) formed by the initial topochemical polymerization[13] of the 3-fold diyne **13a**.

Explosive decomposition with the loss of crystal solvent (dichloromethane/hexanes) seems to be coupled. No discrete DSC signal was recorded for the evaporation of crystal solvent. Explosive decomposition commences with single crystalline material but not with precipitated powders, suggesting that the preorganization of the π-system is important.[21] The supramolecular order and *not* the intrinsic strain within the molecular structure plays a major role in the explosive formation of the nanostructures.[10,21] The likely reason for the explosion of **13a**

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(24) It is difficult to estimate yields by TEM but the ring-shaped nanostructures are almost everywhere. For a low magnification picture that gives an impression of the abundance of the nanostructures, see the Supporting Information.

is the uniquely close contact of the butadiyne units in the solid state because of the absence of bulky ring substituents.[21] These contacts tighten upon loss of crystal solvent (Figure 2) with considerable compaction/collapse of the lattice, ultimately leading to the observed carbon nanostructures.

Conclusions

A series of eight novel organometallic dehydro[18]annulenes **10** and **13** was prepared by a combination of standard Pd- and Cu-catalyzed couplings. These compounds pyrolyze from 183 to 293 °C. In the cycle **13a**, the explosive thermal decomposition furnishes carbon nanomaterials with a rope- or onion-like internal structure. Currently, we are investigating the introduction of heteroatoms into organometallic dehydro[18]annulenes. We will study how the presence of heteroatoms will affect the formation and structures of the explosion-generated carbon nanostructures.

Acknowledgment. We thank the National Science Foundation (Bunz, CAREER, CHE 9981765) and the USC NanoCenter for generous funding. UB is a Camille Dreyfus Teacher-Scholar (2000-2004). We thank Dr. D. Dunkelberger for help with the electron microscopy, Dr. J. Selegue and Dr. F. E. Huggins (U of Kentucky) for valuable discussions and a Mössbauer spectrum of the soot formed from **13a**.

Supporting Information Available: Experimental procedures, detailed spectroscopic characterization, and crystallographic information files [CIFs for **10b** (CCDC 162440), **10d** (CCDC 162301), **10e** (CCDC 162305), **13a** (CCDC 162304), **13b** (CCDC 162303)] are available free of charge via the Internet at http://pubs.acs.org.

JA026809O