

# Hexa-*peri*-hexabenzocoronenes by Efficient Oxidative Cyclodehydrogenation: The Role of the Oligophenylene Precursors

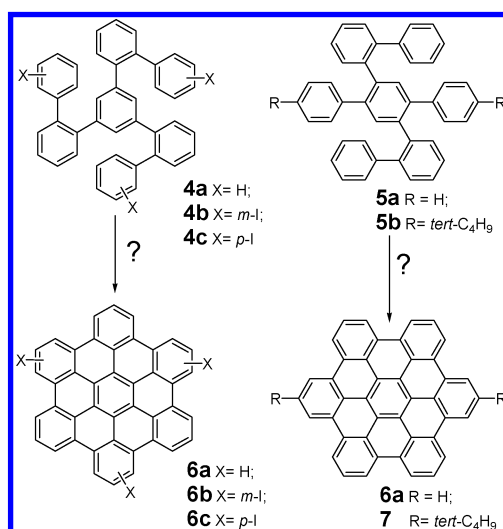
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## ABSTRACT



Oligophenylene precursors based on 1,3,5-tris-(2'-biphenyl)ylbenzene (**4a**) and 1,4-bis-(2'-biphenyl)yl-2,5-diphenylbenzene (**5a**) were prepared and utilized for efficient hexabenzocoronene (HBC) synthesis by cyclodehydrogenations. Parent HBC **6a** was efficiently synthesized from the 1,3,5-tris-(2'-biphenyl)ylbenzene precursor, and novel *D*<sub>3h</sub> symmetrical HBCs were prepared from 1,3,5-tris-(2'-biphenyl)ylbenzenes with various substitution types. For the preparation of a *tert*-butyl containing HBC **7** with *D*<sub>2h</sub> symmetry, a two-step cyclodehydrogenation was required because of changes in the spin density distribution.

Polycyclic aromatic hydrocarbons (PAHs) have continuously attracted the interest of organic chemists and materials scientists because of their large  $\pi$ -systems and strong  $\pi$ -stacking that have led to one-dimensional charge-transporting channels.<sup>1</sup> Pioneering syntheses of PAHs were

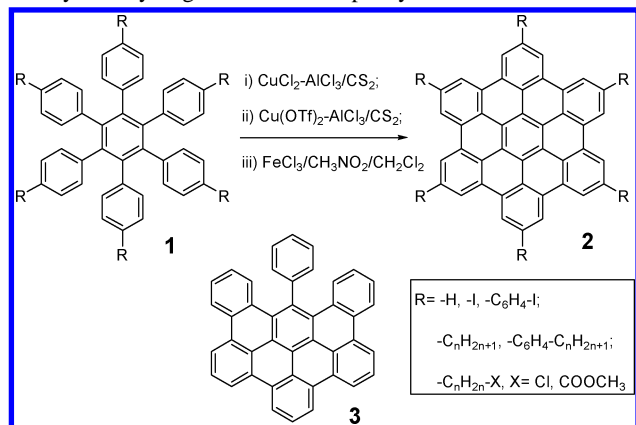
performed by Scholl and Clar et al. under harsh conditions.<sup>2</sup> Well-defined HBCs and their higher homologues show high thermal and chemical stability and serve as useful organic semiconductors in electronic and optoelectronic devices.<sup>3</sup> However, previous synthetic methods have afforded HBCs

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in very low yields.<sup>4</sup> Our group has developed an efficient way for preparing a variety of HBCs **2** through a mild intramolecular oxidative cyclodehydrogenation of hexaphenylbenzene precursors **1** (Scheme 1).<sup>5</sup> Several suitable

**Scheme 1.** General Synthesis of HBCs by Oxidative Cyclodehydrogenation of Hexaphenylbenzene Precursors

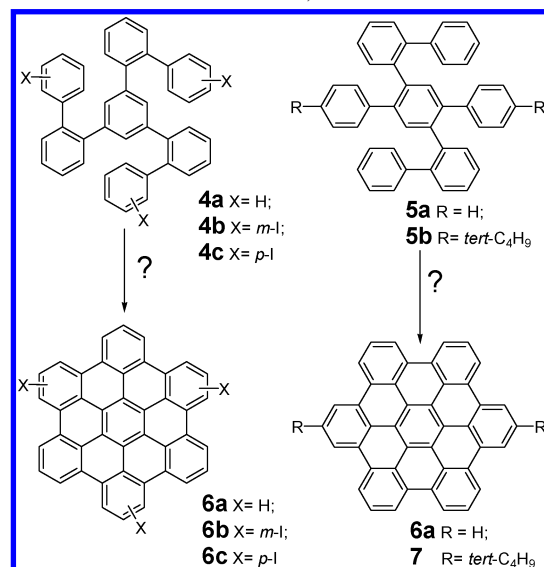


oxidant systems have been utilized for these transformations including  $\text{CuCl}_2/\text{AlCl}_3$ ,  $\text{Cu}(\text{OTf})_2/\text{AlCl}_3/\text{CS}_2$ , and  $\text{FeCl}_3/\text{CH}_3\text{NO}_2$ . Through detailed studies of the oxidative cyclodehydrogenation, the parent hexaphenylbenzene (HPB) was found to exclusively cyclodehydrogenize in an intramolecular fashion. Furthermore, the intermediate phenyldibenzo[fg,ij]-phenanthro[9,10,1,2,3-pqrst]pentaphene (**3**) could be separated, indicating that the cyclodehydrogenation proceeded in a stepwise process.<sup>6</sup> Recently, theoretical studies have pointed toward a radical cation mechanism for these intramolecular fusion reactions. The geometry, charge, and spin distribution of the radical cation intermediates are decisive for the step-by-step bonding formation mechanism.<sup>7</sup>

HPBs can be synthesized by the cyclotrimerization of diphenylacetylene or the Diels–Alder reaction between diphenylacetylene derivatives and tetraphenylcyclopentadienones.<sup>8</sup>  $D_{6h}$  symmetric or unsymmetric HBC molecules with iodo, iodophenyl, alkyl, and alkylphenyl substitutions have

been synthesized, and functional groups such as esters at the end of aliphatic chains can also be introduced. However, the synthesis of HBC molecules with lower symmetry such as  $D_{3h}$  met with difficulties.<sup>9</sup> In addition, the cyclodehydrogenation of HPB precursors is sometimes limited by the electron-rich and -poor characters of the substitutions.<sup>10</sup> To broaden the scope of HBC analogues, we have found the use of other oligophenylene precursors such as 1,3,5-tris-(2'-biphenyl)benzene (**4**) or 1,4-bis-(2'-biphenyl)yl-2,5-diphenylbenzene (**5**) (Scheme 2). Although they differ from HPBs

**Scheme 2.** Potential Synthesis of HBCs from Precursors **4a–c** and **5a,b**



in topology, they can undergo similar intramolecular cyclodehydrogenations to afford HBC molecules. Following this concept, here we describe an efficient synthetic method for the preparation of known HBCs (including **6a**) and unknown derivatives such as iodo compounds **6b,c** and the  $D_{3h}$  or  $D_{2h}$  symmetric species **7**.

As shown in Scheme 3, 1,3,5-tris-(2'-bromophenyl)-benzene (**9**) was synthesized in 72% yield by trifluoromethanesulfonic-acid-mediated trimerization of 2-bromoacetophenone (**8**). It is worthy to note that other Lewis acids typically used for condensation trimerizations of substituted acetophenones such as  $\text{SiCl}_4$  and  $\text{TiCl}_4$  were ineffective or problematic.<sup>11</sup> Molecule **9** constitutes an important building block for subsequent palladium-catalyzed

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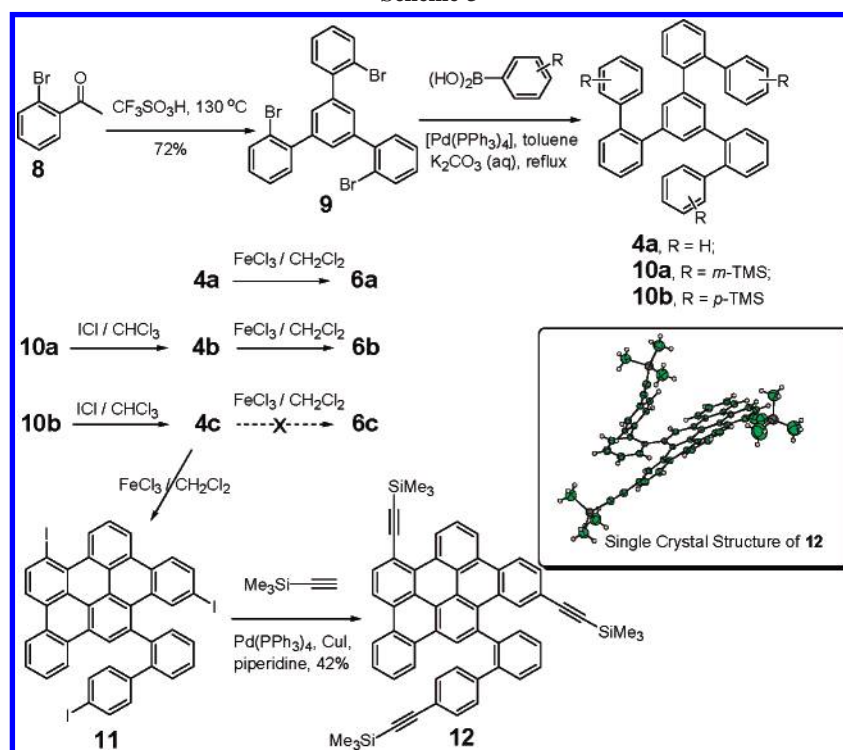
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Scheme 3



Suzuki, Stille, and Negishi coupling reactions and in our study led to various 1,3,5-tris-(2'-biphenyl)ylbenzene structures. Suzuki coupling of **9** with phenylboronic acid, 3-trimethylsilyl-1-phenylboronic acid, and 4-trimethylsilyl-1-phenylboronic acid afforded **4a**, **10a**, and **10b** in 86%, 90%, and 93% yields, respectively. Comparatively, it should be noted that **10a** was previously synthesized by a three-step procedure in only 48% yield.<sup>9</sup> The trimethylsilyl groups in **10a** and **10b** were then converted into iodo groups by treatment with iodine monochloride and gave **4b** and **4c** in 92% and 93% yields, respectively.

The intramolecular oxidative cyclodehydrogenation reactions were then performed on compounds **4a–c** using  $\text{FeCl}_3$  as an oxidant. The parent HBC **6a** was obtained as yellow powder in 80% yield from compound **4**. The MALDI-TOF mass spectra of the product revealed that no chlorination had occurred during this cyclodehydrogenation process, even after prolonged reaction times up to several hours. This result is important because chlorination was frequently observed with HPB cyclodehydrogenations<sup>5b,12</sup> and suggests that the present synthesis of parent HBC is superior. It also appears that the topology of the precursor plays an important role for cyclodehydrogenation. Likewise, compound **6b** can be prepared from **4b** under similar conditions and provides a useful building block for further functionalization.<sup>9</sup> Interestingly, the similar cyclodehydrogenation reaction of **4c** did not afford completely planarized HBC **6c**, even after

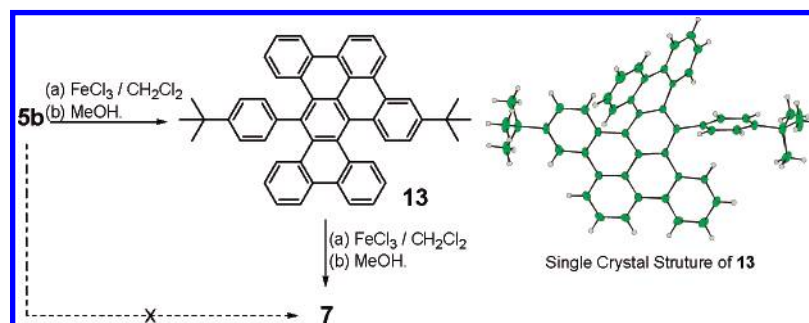
prolongation of the reaction time up to 23 h. The MALDI-TOF mass spectrum of the obtained insoluble, yellow powder showed only a single species with a molecular ionic peak at 905, suggesting that only six hydrogen atoms had been removed. The poorly soluble compound **11** was then reacted with trimethylsilylacetylene under Hagihara–Sonogashira conditions to give a single soluble product **12**, whose structure could be confirmed by single-crystal structure analysis.<sup>13</sup> The crystal structure (Scheme 3, inset) clearly shows that the biphenyl group of **12** is highly twisted out of the central plane and has a dimeric oblique packing mode (for details in a CIF file, see Supporting Information). Therefore, structure **11** was ascribed to the insoluble yellow powder where one of the biphenyl units had not formed new C–C bonds during the reactions. This result further supports a stepwise cyclodehydrogenation mechanism proceeding from **4a–c** to **6a–c**. We believe the reason that **4c** can only be partially closed is due to the steric hindrance induced by the twist of the biphenyl units and the poor solubility of the product.

Encouraged by the efficient cyclodehydrogenation of 1,3,5-tris-(2'-biphenyl)ylbenzene precursors, we revisited a previously failed reaction, namely the cyclodehydrogenation of **5b** to compound **7**.<sup>14</sup> In this study, we carefully controlled the quantity of oxidant and the reaction time. Interestingly,

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(13) Crystals suitable for X-ray structure analysis were obtained by slow evaporation of a  $\text{CH}_2\text{Cl}_2$  solution of compounds **12** and **13** at room temperature. Crystal structure determination was carried out on a KCCD diffractometer with graphite-monochromated Mo  $\text{K}\alpha$  irradiation. The structure was solved by direct methods (SHELXS-97).

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Scheme 4. Oxidation of **5b**

cyclodehydrogenation of **5b** by treatment with  $\text{FeCl}_3$  in dichloromethane over 30 min and up to 5 h only yielded a partially closed intermediate **13**, which was again supported by single-crystal analysis (Scheme 4).<sup>15</sup> Alternatively, the analogue species, 1,4-bis(2'-biphenyl)yl-2,5-diphenylbenzene (**5a**), afforded complex mixtures under the same oxidations. Comparing these two examples, we then ascribed that the *tert*-butyl groups in precursor **5b** stabilize the intermediate cation radical during the dehydrogenation process. This stabilizing effect in turn does not allow further cyclization and complete planarization to form HBC **7**. The stable cation radical of **13** was quenched by adding methanol to afford **13** in 68% yield. To support our hypothesis of cation radical stabilization, compound **13** was then further submitted to the oxidative cyclodehydrogenation by using 12 equiv of  $\text{FeCl}_3$  for 30 min. Amazingly, completely closed HBC molecule **7** was obtained in quantitative yield and without any chlorination! Therefore, two independent cyclodehydrogenations must be performed to clearly transform **5b** into **7**.

In conclusion, parent HBC **6a** was successfully synthesized from the 1,3,5-tris-(2'-biphenyl)ylbenzene precursor using

typical cyclodehydrogenation conditions. The new synthetic method starting from 1,3,5-tris-(2'-bromophenyl)benzene offers opportunities for synthesizing novel HBC derivatives, especially  $D_{3h}$  symmetric HBCs that can otherwise not be obtained from typical hexaphenylbenzene precursors. The attachment of *tert*-butyl groups helps to change the spin density distribution and therefore requires a two-step procedure to prepare its HBC analogues. The partially cyclodehydrogenized products can be separated and characterized, further suggesting a stepwise ring-closing mechanism including radical cations.

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**Supporting Information Available:** Full experimental details, the MALDI-TOF mass spectra of compounds **7** and **11**, and crystallographic information files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) For crystal growth, see ref 13.