Carbocycles

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Dibenzopentalenes from $B(C_6F_5)_3$-Induced Cyclization Reactions of 1,2-Bis(phenylethynyl)benzenes**

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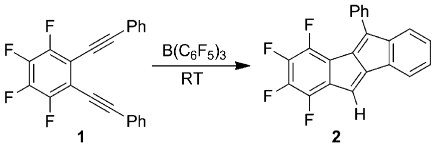
Dibenzopentalene derivatives are compounds with extended π systems which have been of great interest in organic materials science with regard to their electronic properties.[1] A variety of synthetic entries to this class of compounds has been described, including classical group transformation chemistry,[2,3] radical coupling,[4,5] and metal-induced reactions.[6–10] We have now found that dibenzopentalenes can be formed by $B(C_6F_5)_3$-induced intramolecular alkynyl coupling reactions.

In a first experiment we treated 1,2-bis(phenylethynyl)-tetrafluorobenzene (**1**) with $B(C_6F_5)_3$ (one molar equiv) in dichloromethane (−20 °C→RT, 2 d). Workup, including column chromatography, eventually gave compound **2** as a red solid in 58 % yield (Scheme 1).[11] The product **2** was characterized by X-ray diffraction (single crystals were obtained from CH_2Cl_2; Figure 1). The data showed that **1** had been isomerized to its dibenzopentalene isomer **2**, which features the typical alternating double and single bonds at its central bicyclic core. In solution we observed the ^{1}H NMR resonance of the single C*H* proton at the central pentalene core at $\delta = 6.60$ ppm ($J_{FH} = 2.3$ Hz). The ^{13}C NMR signals of the four core sp^2-carbon atoms are found at $\delta = 118.0$ (CH), 150.2, 139.0, and 146.7 ppm, respectively, and we observed four distinct ^{19}F NMR signals for **2** ($\delta = -131.0$, -159.5, -158.6, -146.0 ppm).



Scheme 1. Formation of the unsymmetric dibenzopentalene derivative **2**.

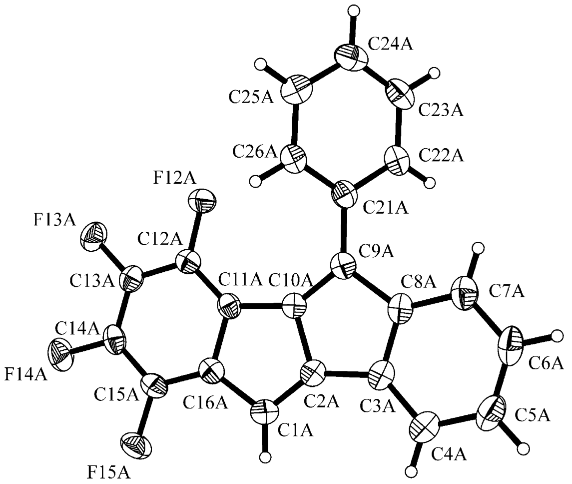


Figure 1. Molecular structure of the dibenzopentalene derivative **2**. Selected bond lengths [Å] and angles [°]: C1A–C2A 1.349(3), C2A–C3A 1.470(3), C3A–C8A 1.413(3), C8A–C9A 1.503(2), C9A–C10A 1.365(2), C10A–C11A 1.465(2), C11A–C16A 1.428(2), C1A–C16A 1.468(2), C2A–C10A 1.457(2); C1A-C2A-C10A 111.2(2), C2A-C10A-C9A 110.6(2). Only one of the two independent molecules in the asymmetric unit is shown. Thermal ellipsoids are shown at 50% probability.

The reactions of the bis(phenylethynyl)benzene derivatives **3a**,**b** with $B(C_6F_5)_3$ under similar reaction conditions had a slightly more complex outcome. We isolated a mixture of the three products, **4**, **5**, and **6**; **4a**, **5a**, and **6a** had a combined yield of 68 %, **4b**, **5b**, and **6b** had a combined yield of 92 % (Scheme 2). The products were separated by chromatography and each product was characterized by X-ray diffraction and by spectroscopy (for details see the Supporting Information). The compounds **4a**[10] and **4b** were identified as the dibenzopentalene derivatives (for example, **4b**: pentalene C*H*: $\delta = 6.44$ ppm (^{1}H NMR), $\delta = 126.1$ ppm (^{13}C NMR); see the Supporting Information). The compounds **5a** and **5b** contain the same dibenzopentalene framework as **4**, but in addition to

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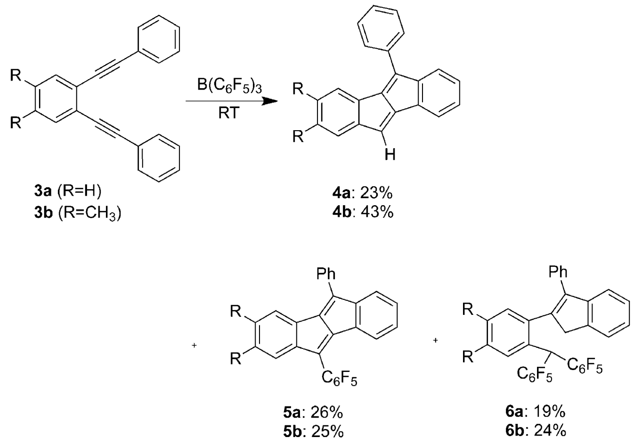


Scheme 2. Formation of **4**, **5**, and **6**.

the single phenyl group at the core they have an additional C_6F_5 substituent, attached at the central pentalene unit, which obviously has been transferred from the $B(C_6F_5)_3$ reagent in the course of the synthetic sequence. The X-ray crystal structure analysis of **5b** shows the planar dibenzopentalene framework to which the phenyl and the newly introduced C_6F_5 groups are bonded (Figure 2).

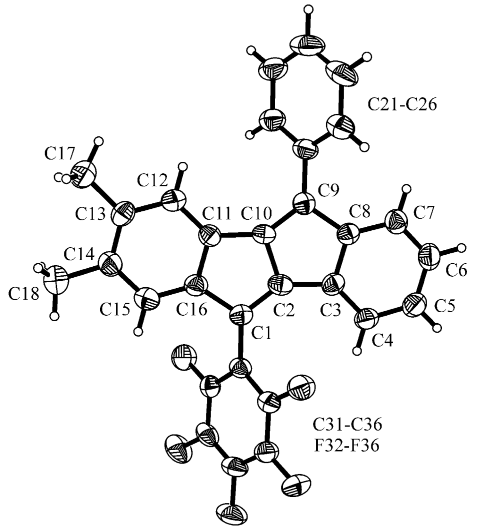
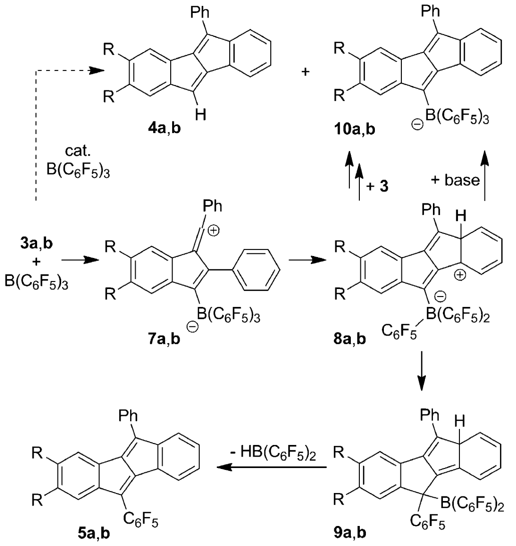


Figure 2. Molecular structure of the dibenzopentalene derivative **5b**. Selected bond lengths [Å] and angles [°]: C1–C2 1.350(3), C2–C3 1.459(4), C3–C8 1.427(3), C8–C9 1.488(4), C9–C10 1.364(3), C10–C11 1.462(3), C11–C16 1.411(3), C1–C16 1.494(4), C2–C10 1.464(3); C1-C2-C10 110.2(2), C2-C10-C9 109.8(2). Thermal ellipsoids are shown at 50% probability.



Scheme 3. Proposed mechanism for the formation of **4** and **5**.

In solution, **5b** exhibits the typical ^{19}F NMR signals of the C_6F_5 substituent ($\delta = -137.0$ (o), -154.4 (p), -162.0 ppm (m)) and the ^1H NMR resonances of the vicinal methyl substituents ($\delta^1H = 2.12$ and 2.10 ppm). The third set of products in this series (**6a**, **b**) contains a geminal pair of C_6F_5 substituents and they do not contain the finished pentalene nucleus. We could show that **6** is not a primary product of this reaction, but likely originates from a hydrolysis reaction during the workup procedure (for details see the Supporting Information).

Scheme 3 provides a possible mechanistic rationalization of the formation of the key compounds **4** (and consequently also **2**) and **5**. We assume that initial $B(C_6F_5)_3$ addition[12] to a carbon–carbon triple bond of the starting material **3** generates the reactive intermediate **7**, which then undergoes an intramolecular electrophilic aromatic substitution reaction to give **8**. Deprotonation of this intermediate by means of proton transfer to the starting material **3** would then give the borylated product **10** and at the same time would open a pathway to the formation of **4**. The latter product in this scheme is consequently suggested to be formed in a $B(C_6F_5)_3$-induced catalytic isomerization reaction of **3**. Competing 1,2-C_6F_5 migration reaction from a boron to carbon atom[13] opens the stoichiometric reaction pathway to the observed co-product **5**. It features the reactive intermediate **9** which then may lose $HB(C_6F_5)_2$ in the rearomatization reaction to eventually give **5**.

The following experimental evidence may serve to support this suggested pathway. We found one case were the isomerization was Brønsted acid catalyzed, namely the **1** to **2** isomerization was achieved by $HN(SO_2CF_3)_2$ catalysis (36% of **2** isolated).[14] The compound **1** also reacted with the Lewis acid BCl_3 to give a BCl_2-substituted dibenzopentalene derivative which was deborylated with acetic acid to eventually also yield **2** (see the Supporting Information). We were able to prepare and isolate the salt **10a** (and **10b**, both with an ammonium counterion) by reacting **3a** with the $B(C_6F_5)_3$/tetramethylpiperidine (TMP) frustrated Lewis pair.[15] In this case the alleged intermediate **8a** was deprotonated by the bulky amine base to give the $TMPH^+$ salt of **10a**. It was isolated in 93% yield and characterized by an X-ray crystal structure analysis (see Figure 3 and the Supporting Information).

We have obtained experimental evidence for the proposed $HB(C_6F_5)_2$ elimination step from the reaction of bis(thienylethynyl)dimethylbenzene (**11**) with $B(C_6F_5)_3$

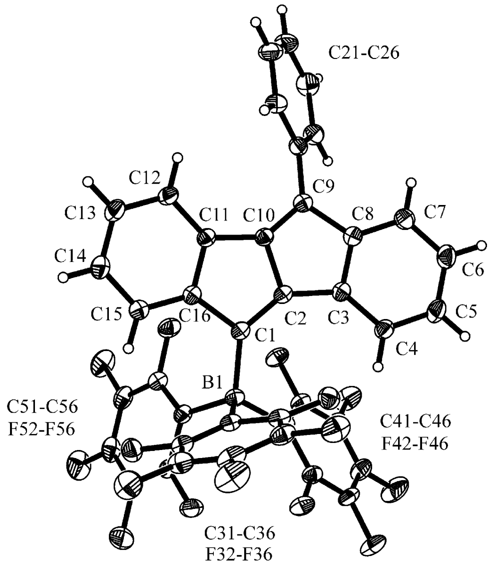


Figure 3. Molecular structure of the dibenzopentalene derivative **10a**. Selected bond lengths [Å] and angles [°]: C1–C2 1.367(6), C2–C3 1.467(5), C3–C8 1.426(5), C8–C9 1.486(5), C9–C10 1.350(6), C10–C11 1.461(5), C11–C16 1.419(6), C1–C16 1.506(5), C2–C10 1.491(5); C1-C2-C10 111.0(3), C2-C10-C9 110.7(3). For clarity only the anion is shown. Thermal ellipsoids are shown at 30% probability.

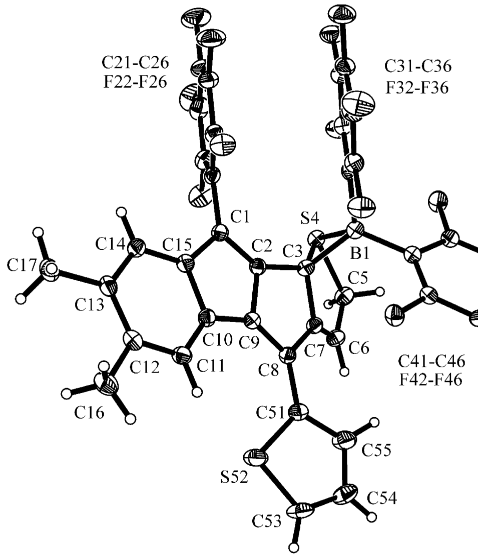
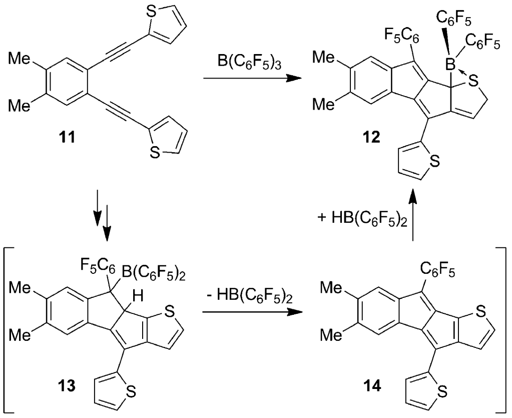


Figure 4. A view of the molecular structure of compound **12**. Selected bond length [Å] and angles [°]: B1–C3 1.590(3), C3–S4 1.876(2), B1–S4 1.988(2), C3–C7 1.509(3), C7–C6 1.329(3), C6–C5 1.501(3), C5–S4 1.840(2); C1-C2-C9 110.3(2), C2-C9-C8 111.2(2). Thermal ellipsoids are shown at 30% probability.



Scheme 4. Formation of **12**.

(1 molar equiv, pentane, RT, 12 h) from which we isolated the product **12** in 90% yield (Scheme 4).[16] It constitutes the $HB(C_6F_5)_2$ addition product to the alleged pentalene derivative **14** which itself was probably formed by the elimination of $HB(C_6F_5)_2$[17] from the respective reactive intermediate **13**, the hetarene analogue of the proposed intermediate **9**. The compound **12** shows the ^1H NMR signals of the geminal pair of dihydrothiophene hydrogen atoms at $\delta = 4.08$ and 3.58 ppm ($^2J = 17.0$ Hz).

Compound **12** was characterized by X-ray diffraction (Figure 4). It shows that $HB(C_6F_5)_2$ has 1,4-hydroborated the annulated thiophene ring of **14**. The angular $B(C_6F_5)_2$ substituent features a strong interaction with the sulfur atom of the dihydrothiophene subunit of **12**. The B1–S4 distance (1.988(2) Å) is even shorter than the B–S bond length in $B(C_6F_5)_3{\cdot}SMe_2$.[18] The sum of the C-B-C bond angles in **12** is 354.7°. Together with the MP2/6-31G* calculated Wiberg bond index[19,20] of 0.72 (see the Supporting Information), these data indicate sulfur coordination to boron.[21] The unusual bonding situation in **12** might be realized by the structural constraint resulting from the ring-fused structure.

The UV/Vis absorption spectra of the dibenzopentalene derivatives **2**, **4a**, and **4b** exhibit three characteristic absorption bands as already reported for dibenzopentalene derivatives:[6] the longest and very weak absorption bands around $\lambda = 500$ nm (attributable to symmetry-forbidden HOMO–LUMO transitions typical for $4n$ π-electron systems[6]), the second longest absorption band with the maximum wavelength of $\lambda = 387$–452 nm, and the third longest absorption bands at $\lambda = 250$–300 nm. The introduction of a C_6F_5 group at the 5-position of dibenzopentalene (i.e., going from **4a** to **5a**, and from **4b** to **5b**) results in the significant bathochromic shifts of the absorption bands. According to the results of DFT calculations, C_6F_5 groups cause a pronounced decrease in the LUMO energy level mainly because of their electron-withdrawing effect (see Figure 5 and the Supporting Information).

Our study shows that readily available 1,2-bis(arylethynyl)benzenes can efficiently be doubly ring closed to yield dibenzopentalene products upon treatment with the strong Lewis acid $B(C_6F_5)_3$ under mild reaction conditions. We have found that the overall sequential reaction scheme follows two competing pathways, thus leading to either the dibenzopentalene isomers of the starting materials (e.g. **2** or **4**) or to the C_6F_5-substituted dibenzopentalenes, which involves substituent transfer from the Lewis acid to the newly formed annulated tetracyclic framework. We need to work out measures for generally controlling this competing situation, although we have found examples of highly selective product formation (**2**, **12**), wherein one of the pathways seems to be

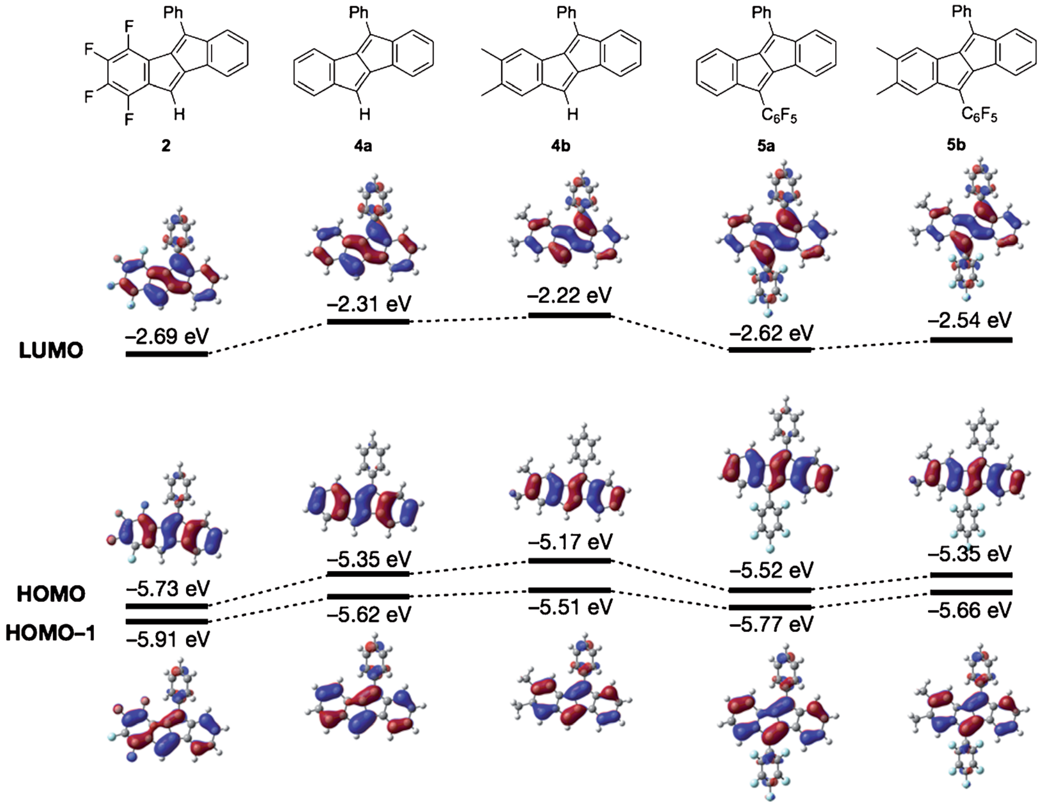


Figure 5. Orbital energy diagram and pictorial representation of HOMO-1, HOMO, and LUMO for the series of dibenzopentalenes **2**, **4a**, **4b**, **5a**, and **5b**; calculated at the B3LYP/6-31G* level (isovalue: 0.03).

highly favored. Thus the boron Lewis acid-induced reaction has the potential to become useful for synthesizing specifically substituted dibenzopentalene derivatives which are difficult to make by conventional means.

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[11] Preparation of **2**: $B(C_6F_5)_3$ (256 mg, 0.5 mmol) was dissolved in dichloromethane (−20 °C, 10 mL) and added to a solution of the diyne **1** (175 mg, 0.5 mmol) in dichloromethane (−20 °C, 10 mL). The resulting dark-green reaction mixture was allowed to warm to room temperature and stirred for 2 days before ether (p.a., 5 mL) was added. Then all the volatiles were removed under vacuum and the residue was purified by column chromatography (SiO_2, cyclohexane:dichloromethane = 20:1). The product was obtained as a red solid (102 mg, 0.29 mmol 58 %).

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[16] Preparation of **12**: **11** (50 mg, 157 μmol, 1 equiv) was dissolved in dry *n*-pentane (5 mL). Then a solution of $B(C_6F_5)_3$ (80 mg, 157 μmol, 1 equiv) in dry *n*-pentane (5 mL) was added at room temperature. The reaction mixture turned red-brown immediately. The mixture was stirred overnight. Subsequently the supernatant of the suspension was decanted by pipette and the obtained residue was washed with *n*-pentane (3 × 2 mL). After drying in vacuo a brown solid was obtained (90 %, 117 mg, 141 μmol).

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