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Aryl–Aryl Coupling

Facile Bucky-Bowl Synthesis by Regiospecific Cove-Region Closure by HF Elimination**

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Rational synthesis of geodesic structures is of great interest, in particular as a promising method for the synthesis of individual fullerene isomers[1] and isomerically pure single-wall carbon nanotubes.[2,3] The strategy generally followed starts with the synthesis of a polycyclic aromatic hydrocarbon (PAH) containing the carbon framework required for the target molecule, which can be rolled up to the desired carbon nanostructure by aryl–aryl domino coupling. The efficiency of such a domino reaction has been demonstrated on the synthesis of I_h-C_{60} and T_d-C_{84} fullerene cages on the Pt(111) surface (Figure 1).[4,5]

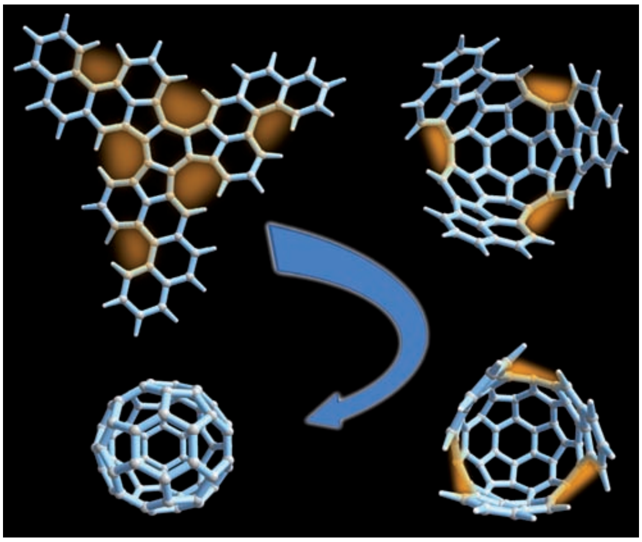

Figure 1. Aryl–aryl domino coupling of the I_h-C_{60} precursor $C_{60}H_{30}$. The cove and fjord regions where the direct aryl–aryl coupling can take place are highlighted in orange. Each subsequent condensation step leads to formation of new cove or fjord regions. Thus, the reaction can proceed in a domino fashion, resulting in the formation of the desired fullerene cage.

Although the platinum-catalyzed cyclodehydrogenation process was found to occur in a highly selective manner, it is limited to only picomole amount production. Alternatively, the consecutive series of intramolecular condensations can be realized by flash vacuum pyrolysis (FVP).[6] The possibility of selective fullerene cage formation through FVP has been demonstrated at the examples of C_{60}, C_{78}, and C_{84}.[7–9] However, the conversion rates to the target molecules have remained disappointingly low. The presence of halogen atoms, such as chlorine or bromine, in the initial precursor has been found to be essential to initiate such a process. This approach has proven to be prolific for the synthesis of many small buckybowl structures, but has reached its limits in the case of large molecules.[10–13] Fluorine functionality was found to be a good alternative.[11,14–16] Owing to its low atomic weight and small size, the fluorine atom can be rather easily introduced in the sterically hampered cove regions. Moreover, high chemical resistance of the C–F bond extends the scope of reactions that can be applied for the precursor synthesis remarkably.[16] Previously we have demonstrated the possibility of selective intramolecular ring closure by HF elimination with FVP.[15] Nevertheless, the conversion rate was found to be still too low (about 60% for a single cyclization) to carry out a multifold process effectively. Apart from modest yield and difficulty in scale-up, the main drawback of the FVP technique is minimum functional group tolerance and numerous side reactions caused by the harsh reaction conditions. To overcome these disadvantages, several alternative liquid-phase intermolecular aryl–aryl coupling techniques have been developed. Here the palladium(0)-catalyzed direct arylation utilizing bromo and chloro derivatives or aryl triflates has been found to be effective for the synthesis of small buckybowls.[17–20] Unfortunately, this method can hardly be extended to fluorinated precursors, which are expected to be significantly less reactive than chlorinated and brominated analogues. Furthermore, the main drawback of the approach is aggressive reaction conditions with respect to the fullerene species.[21] The discovery of C–F bond activation under transition-metal-free conditions utilizing silylium carborane catalysis might be a solution to this problem.[22] Recently Siegel et al. have successfully applied this methodology to intramolecular aryl–aryl coupling.[23] Unfortunately, the remarkable decrease in yield in the case of nonplanar PAHs, which already drops from 99% to 50–80% for single condensation, limits its application for multifold reactions. It is worth mentioning that all solution approaches might be not effective in the case of large PAHs, which are typically highly insoluble compounds. Moreover, the intramolecular aryl–aryl coupling cannot be realized in a domino fashion by palladium(0)-catalyzed direct arylation or by silylium carborane catalysis.

In the search for a more effective method for ring closure that is applicable for highly insoluble fullerene precursors, we have turned our attention to solid-state catalysis. Herein, we

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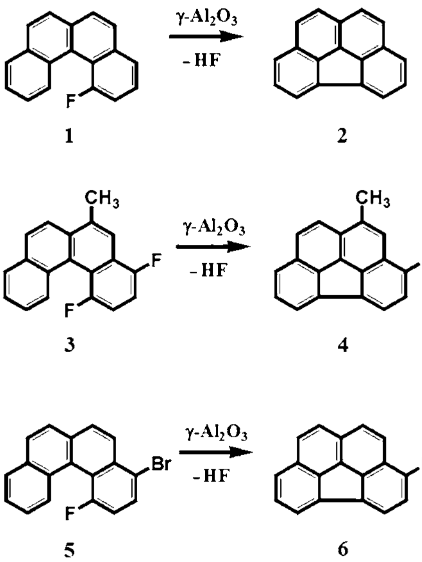
present an efficient cove-region closure process (CRC) realized by regiospecific HF elimination. Apart from the simplicity and high reproducibility, the described technique avoids all of the abovementioned limitations. Examination of the CRC approach for synthesis of buckybowl structures has demonstrated an unprecedentedly high selectivity and conversion level.

The conversion of 1-fluorobenzo[*c*]phenanthrene (**1**) to benzo[*ghi*]fluoranthene (**2**) was chosen as a model reaction for the investigation. Benzo[*c*]phenanthrene is the smallest molecule that can have a cove region where the new bond should be established (Scheme 1). It was found that γ-Al_2O_3 displays pronounced activity in ring closure in **1**, which starts above 300 °C. In the case of benzo[*ghi*]fluoranthene, the high temperature does not cause further decomposition and **1** can be converted into **2** effectively. Nevertheless, the conditions are too harsh for buckybowl synthesis. During the optimization of the condensation conditions, it was discovered that the high temperature is only required for γ-Al_2O_3 activation, whereas the condensation process can proceed smoothly at lower temperatures. The best results were obtained after activation of γ-Al_2O_3 by annealing at 500 °C for 15 min at 10^{-3} mbar pressure. Using such activated γ-Al_2O_3, compound **1** can be quantitatively transformed to **2** at remarkably low temperatures. Thus, quantitative conversion of **1** into **2** was observed after 20 h at 150 °C. Full conversion has even been achieved at 100 °C after 60 h. The same process can be completed in 1 h or in just several minutes at 200 °C and 250 °C, respectively. For practical purposes, the temperature interval of about 150–200 °C was found to be the most appropriate, as it is low enough to prevent possible product decomposition and high enough to achieve the full conversion in a rather short period of time.



Scheme 1. Cove-region closure (CRC) mediated by Al_2O_3. CRC by HF elimination in 1-fluorobenzo[*c*]phenanthrene derivatives, demonstrating high chemoselectivity and regiospecificity of the process. Compounds **2**, **4**, and **6** were obtained in quantitative or close to quantitative yield.

Further investigations have revealed an unexpectedly high chemoselectivity and regiospecificity of the process. Thus, if the fluorine atom is not involved directly in the cove region (2-fluorobenzo[*c*]phenanthrene), no reaction takes place and the compound remains completely intact. The regiospecificity of the process has been demonstrated on the synthesis of compound **4**, in which cove-region closure in **3** was achieved quantitatively (Scheme 1). Surprisingly, chlorinated and even brominated analogues (2-chlorobenzo[*c*]phenanthrene and 2-bromobenzo[*c*]phenanthrene) remain completely intact under condensation conditions. The high chemoselectivity has been demonstrated by the synthesis of compound **6**, for which HF elimination was achieved in the presence of a C–Br bond in more than 98 % yield. Importantly, no fluorine-to-hydrogen exchange was observed and no evidence of any side reactions was obtained during the CRC process. As monitored by HPLC analysis, the products form exclusively and require no further purification procedure (Supporting Information). Obviously, the driving force of the reaction is the formation of an Al–F bond which is characterized by substantial bond strength. On the other hand, the results obtained exclude direct C–F bond activation and indicate that no reactive intermediates form during the CRC process. The most probable mechanism of the CRC process includes cyclic transition states; that is, the condensation takes place in a concerted fashion (Figure 2). This process seems to be an intermolecular variant of the rare intramolecular dyotropic rearrangement where two sigma bonds migrate simultaneously through a six-electron transition state.[24,25] As bond breaking and bond formation takes place simultaneously no reactive intermediates, which might cause side reactions, form. An aromatic six-electron transition state explains the low activation barrier allowing the reaction to take place under mild conditions. Regiospecificity can also be understood in terms of the assumed mechanism, as 1,2-HF elimination is extremely unfavorable owing to the high energy of benzyne (1,2-didehydrobenzene) species that should be formed in that case. Interestingly, none of the carbon atoms changes hybridization during CRC, which is atypical for an elimination. The formal increase in unsaturation, a necessary prerequisite of any elimination process, is realized through the formation of a new ring in the system.

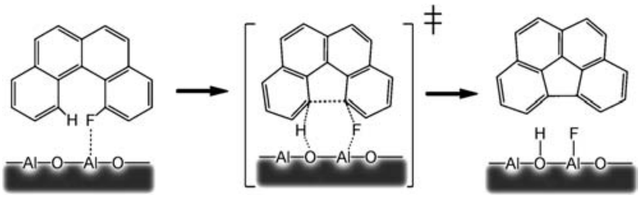


Figure 2. A representation of the most probable mechanism of the CRC for benzo[*c*]phenanthrene condensation, showing the key points of the process: coordination on the aluminum oxide surface, aromatic transition state, and high energy gain owing to Al–F bond formation.

Considering the multifold CRC, it is easy to see that each new pentagon formation imposes additional strain to the system as a result of perturbation of the aromatic system owing to the curvature introduced (Figure 1). Normally, the efficiency of each subsequent condensation step drops remarkably or the condensation process even stops. The suitability of the γ-Al_2O_3-initiated CRC method for construction of nonplanar PAHs has been examined on the synthesis of indacenopicene (**9**), which is known to be stable compound.[26] Despite of the strain imposed, benzopicene **7** was converted into the desired buckybowl **9** quantitatively under mild conditions (150 °C, 60 h). At 250 °C, the same process can be fully completed in 1 h. Interestingly, the product of mono condensation (compound **8**) cannot be detected in the reaction even if the starting material was not fully converted, indicating that the HF elimination in **8** proceeds even faster than in benzopicene **7**. Indacenopicene **9** was obtained in pure form by simple extraction with hot toluene (yield of isolated product 99 %). Single-crystal X-ray analysis unambiguously confirms the structure and reveals the geodesic shape of **9** (Figure 3).

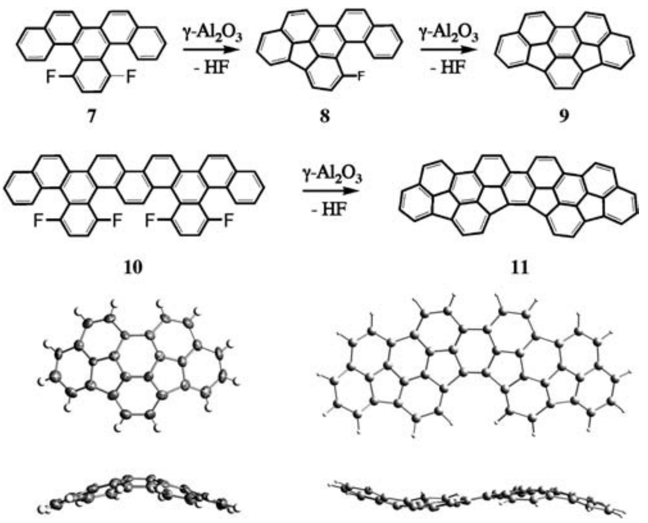


Figure 3. Synthesis of buckybowls by the CRC approach. Top: Buckybowl synthesis by two- and fourfold cove-region closure. Bottom: ORTEP of compound **9** (top and side view) and DFT optimized structure of **11** (top and side view), demonstrating the geodesic shapes. Compounds **9** and **11** were obtained in quantitative yield.

To address the solubility issue we investigated the CRC approach for the badly soluble precursor **10**. It has been found that the fourfold HF elimination can be realized very effectively. After deposition of **10** on an activated γ-Al_2O_3 the mixture was annealed for 10 h at 250 °C. Subsequent Soxhlet extraction with *o*-xylene gave the desired buckybowl **11** in pure form as a hardly soluble red powder (yield of isolated product 98 %). No side products and no products of partial condensation were found in the sample as indicated by HPLC, MS, and NMR analysis (Supporting Information).

In summary, a highly effective solid-state strategy for regiospecific aryl–aryl coupling (cove-region closure) by HF elimination is presented. The efficiency of the approach has been demonstrated by quantitative transformation of precursor molecules to the desired buckybowl structures. Taking into consideration that fluorine can promote the desired ring closure only if a hydrogen atom is neighboring in space in the precursor structure, it seems to be possible to fully control the process and carry out the condensation in domino fashion. The high conversion level into extended buckybowl **11**, which formally represents more than 75 % of the C_{60} fullerene connectivity, demonstrates high potential of the CRC technique for generating extended nonplanar carbon based nanostructures, including higher fullerenes, giant buckybowls, and nanotubes. The high tolerance to chlorine and bromine functionalities makes the CRC approach a very powerful synthetic method for synthesis of functionalized buckybowls, which are useful building blocks for the construction of complex carbon-based nanostructures. In general, our finding shows that the C−F bond, which is widely believed to be the most passive functionality, can be reconsidered as a useful functional group allowing very effective C−C bond formation.

Experimental Section

Cove-region closure experiments were carried out using commercially available aluminum oxide (activated, neutral, 50–200 micron, Acros). Typically, γ-Al_2O_3 (2–3 g) was placed in glass ampule and activated by annealing at 500 °C for 10–15 min in vacuum (10^{-3} mbar). The respective fluoroarene (20–50 mg) was mixed with activated aluminum oxide under argon atmosphere. The ampule was evacuated (10^{-3} mbar) and sealed. The condensation was carried out at 150–200 °C for 2–10 h. The corresponding product was obtained after extraction with toluene (xylene). Synthesis procedures, HPLC chromatograms, MS, NMR, and UV/Vis spectra of all of the new compounds and crystallographic data for compound **9** can be found in Supporting Information. CCDC 860433 (**9**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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