Irradiation of a solution of 5,6,11,12-tetrahydrodibenzo[α,ε]cyclooctatetraene (1) and (RCp)Rh(C₅H₅)₂ under argon atmosphere afforded in a one-pot reaction the Rhodium stabilized [4.8]₃cyclacenes 3 – 7 (Scheme 1).

Scheme 1: One-pot synthesis of Rhodium stabilized [4.8]₃cyclacenes 3 – 7

By means of X-ray diffraction studies on single crystals of 3 – 7, we were able to confirm the hoop shaped structures, providing a conjugated π-system for the central scaffold. In scheme 2 is shown the crystal structure of cyclacene 3 as a representative for this type of compounds.

Scheme 2: Crystal structure of cyclacene 3.

Oligomers of lower or higher molecular weight could not be observed. The reaction mechanism of the formation of the [4.8]₃cyclacenes could be enlightened by isolation of the intermediate 2 (M=Co) after the complexing of the two terminal triple bonds with MeReO₃. The intramolecular distance between the two complexed triple bonds amounts to 4.1 Å. This close proximity favors strongly the formation of [4.8]₃cyclacenes.

Direct synthesis of diyne 12 should deliver further understanding of the reaction mechanism as well as the access to oligomers of lower or higher molecular weight (Scheme 3).
The precursors 8 – 11 were synthesized in eight synthesis steps and the bisselenadiazole 13 in 13 synthesis steps. These compounds were all obtained in satisfactory yields. However, the introduction of cyclic alkynes by decomplexation of the rhenacyclopropenes 8 – 11 or by fragmentation of the bisselenadiazole 13 failed due to the additionally induced ring strain.

In the theoretical part of this work several DFT calculations (B3LYP/6-31G*) on novel cyclacenes as entities consisting of six-membered rings with heteroatoms were presented such as 14, 15, 16 and 18 or eight-membered-rings such as 17 (Scheme 4).

The relative energies and the structural properties derived from this method revealed that these species should be thermodynamically stable at room temperature. Due to the torus shape of the molecules the conjugation is reduced in comparison to a planar ribbon.

**List of Publications**


Gleiter, Rolf; Esser, Birgit; Kornmayer, Stefan C., Cyclacenes: Hoop-Shaped Systems Composed of Conjugated Rings, *Accounts of Chemical Research* 2009, 42(8), 1108-1116.

