

### Introduction:

Benzobarrelenes are bicyclic strained olefins with interesting electronic properties and reactivity as a result of the combination of an aromatic and a barrelene framework.[1-3] Several studies on the reactivity of this type of molecules have been reported and different synthetic strategies were developed for substituted benzo-barrelenes since the first publication on benzobicyclo[2.2.2]-2,5,7-octatriene.[4-7] Interesting derivatives are the tetrafluorobenzobarrelenes, the coordination behavior of which were studied in detail several years ago.[8] However, only recently the catalytic activity of these tetrafluoro-benzobarrelene derivatives was published.[9, 10] Nevertheless, efficient synthetic routes towards benzo-barrelenes bearing substituents at the aromatic ring, which allow further functionalization are still scarce. Here we present a novel synthetic strategy towards such functionalized benzobarrelenes starting from arynes and benzenes. This Diels-Alder type synthesis route starting from stable Grignard reagents, which allow the controlled release of arynes, gives access to a large number of achiral and chiral benzobarrelenes, respectively. Here, the coordination behavior of these molecules as well as the functionalization of the dibromobenzobarrelenes to give carboxylic and phosphonic acid esters is reported and the catalytic activity of selected rhodium complexes is shown.

### Synthetic concept towards a variety of benzobarrelene derivatives

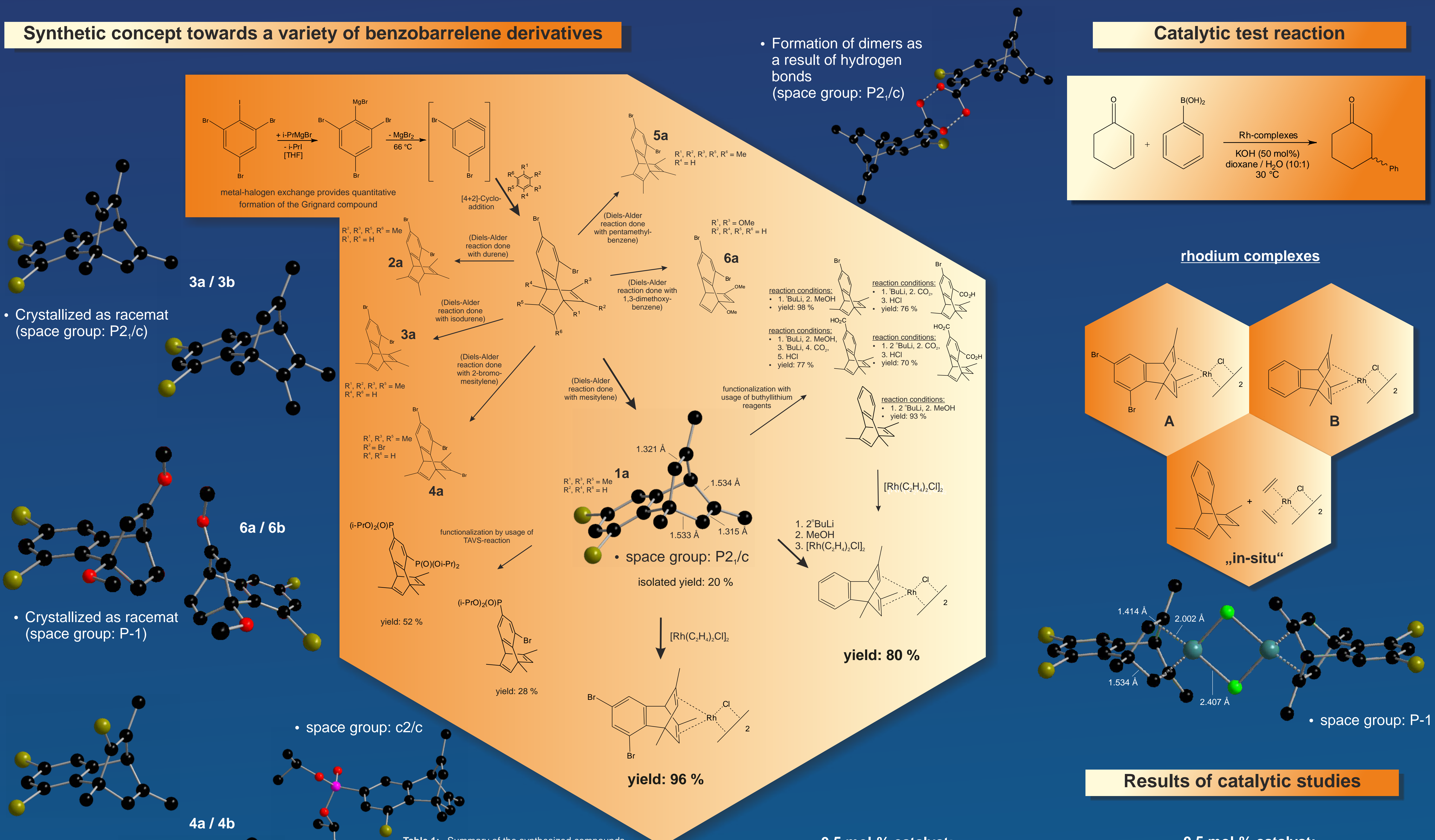


Table 1: Summary of the synthesized compounds 1-6 and yields based on NMR.

compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>	yield <sup>a</sup>
1a	CH <sub>3</sub>	H	CH <sub>3</sub>	H	CH <sub>3</sub>	H	50
1b	H	CH <sub>3</sub>	H	CH <sub>3</sub>	H	CH <sub>3</sub>	15
2a	H	CH <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	28
2b	CH <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	H	16 <sup>b</sup>
2c	CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	16 <sup>b</sup>
3a	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	H	43 <sup>b</sup>
3b	CH <sub>3</sub>	H	CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	19 <sup>b</sup>
3c	H	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	19 <sup>b</sup>
3d	H	CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	19 <sup>b</sup>
4a	CH <sub>3</sub>	Br	CH <sub>3</sub>	H	CH <sub>3</sub>	H	10 <sup>b</sup>
4b	CH <sub>3</sub>	H	CH <sub>3</sub>	H	CH <sub>3</sub>	Br	6 <sup>b</sup>
4c	H	CH <sub>3</sub>	Br	CH <sub>3</sub>	H	CH <sub>3</sub>	31
4d	H	CH <sub>3</sub>	H	CH <sub>3</sub>	Br	CH <sub>3</sub>	14
5a	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	13 <sup>b</sup>
5b	H	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	64 <sup>b</sup>
5c	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	12 <sup>b</sup>
5d	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	
6a	OCH <sub>3</sub>	H	OCH <sub>3</sub>	H	H	H	
6b	OCH <sub>3</sub>	H	H	H	OCH <sub>3</sub>	H	
6c	H	OCH <sub>3</sub>	H	OCH <sub>3</sub>	H	H	
6d	H	H	H	OCH <sub>3</sub>	H	OCH <sub>3</sub>	

<sup>a</sup> The yield was determined based on the NMR data of the crude product.  
<sup>b</sup> The products were obtained as racemic mixtures.

### Summary and Conclusion:

- Novel synthetic route towards dibromobenzobarrelenes including chiral derivatives is reported
- Formation of regio- and stereoisomers as a result of the Diels-Alder reaction mechanism
- Influence on electronic properties of the dien component in regard to conversion, regio- and stereochemistry is shown
- Functionalization at the barrelene framework is possible as demonstrated for the derivative which was obtained by the reaction with 2-bromomesitylene
- Selective metal-halogen exchange is possible synthesis of three different carboxylic acids
- Dicarboxylic acid and phosphonic acid ester derivatives are accessible novel ligands for coordination polymers and metal-organic frameworks
- Potential of benzobarrelenes as diene ligands in coordination chemistry is demonstrated
- Catalytic activity of the halogen-free benzobarrelene rhodium complexes is shown (see catalytic studies)

### conclusion of the catalytic studies:

- catalyst B (halogen-free benzobarrelene rhodium complex) provides quantitative conversion after 12 hours
- bromo-substitution at the benzobarrelene derivative (catalyst A) decreases the catalytic activity (no significant increase in conversion after 12 hours)
- catalyst prepared „in-situ“: longer reaction times required, but quantitative conversions after 12 hours

### outlook:

- functionalization of the dibromobenzobarrelene derivatives to immobilize the catalysts › heterogeneous catalysis
- separation of chiral benzobarrelene derivatives › asymmetric catalysis

### Literature:

[1] H. E. Zimmerman, R. S. Givens, R. M. Pagni, *J. Am. Chem. Soc.* **1968**, *90*, 6096. [2] M. Balci, O. Cakmak, T. Hokelek, *J. Org. Chem.* **1992**, *57*, 6640. [3] K. Beck, S. Hünig, *Angew. Chem. Int. Ed.* **1986**, *25*, 187. [4] R. G. Miller, M. Stiles, *J. Am. Chem. Soc.* **1963**, *85*, 1798. [5] D. J. Berry, B. Wakefield, *J. Chem. Soc. C* **1969**, 2342. [6] N. J. Hales, H. Heaney, J. H. Hollinshead, R. P. Sharma, *Tetrahedron* **1995**, *51*, 7403. [7] L. Pu, R. H. Grubbs, *J. Org. Chem.* **1994**, *59*, 1351. [8] M. A. Esteruelas, L. A. Oro, *Coord. Chem. Rev.* **1999**, *193-5*, 557. [9] T. Nishimura, T. Kawamoto, M. Nagaosa, H. Kumamoto, T. Hayashi, *Angew. Chem. Int. Ed.* **2010**, *49*, 1638. [10] R. Shintani, M. Takeda, T. Nishimura, T. Hayashi, *Angew. Chem. Int. Ed.* **2010**, *49*, 3969.

### Acknowledgements:

We like to thank Prof. Dr. H. Lang (TU Chemnitz), Dr. M. Schürmann and K. Jurkschat (TU Dortmund) for support of this work (X-ray).