

Some Construction Principles in the Development of New Molecular Catalysts.

Lutz H. Gade

*Anorganisch-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany).*

Despite the importance of homogeneous catalytic processes and an ever growing insight into their reaction mechanisms, targeted catalyst development remains a great challenge. This is due to the complexity of the reaction sequences involved and the resulting large number of variables to be considered. Nevertheless, the search for new efficient catalysts and their mechanistic study may be occasionally simplified by consideration of a few structural principles. This situation will be illustrated for several case histories:

These will address inter alia the challenge of *developing stoichiometric reactions to catalytic processes* as is shown for the zirconium catalyzed synthesis of indoles from alkynes and hydrazines.^[1]

The *exploitation of molecular symmetry* in the development of ligands for enantioselective catalysis will be illustrated for C_2 -chiral pincer ligands^[2] and C_3 -chiral trisoxazolines.^[3]

The fact that *multiple reaction pathways* may be associated with apparently simple catalytic transformations becomes evident in studying the Rh-catalyzed hydrosilylation of ketones.^[4]

Finally, the problem of identifying the catalytically active species will be *illustrated for 1,2-dioxygenations of alkenes*.^[5]

- [1] a) T. Gehrman, J. Lloret Fillol, S. Scholl, H. Wadepohl, L. H. Gade, *Angew. Chem. Int. Ed.* **2011**, *50*, 5757; b) T. Gehrman, S. A. Scholl, J. Lloret Fillol, H. Wadepohl, L. H. Gade, *Chem. Eur. J.* **2012**, *18*, 3925.
- [2] a) B. K. Langlotz, H. Wadepohl, L. H. Gade, *Angew. Chem. Int. Ed.* **2008**, *47*, 4670; b) Q.-H. Deng, H. Wadepohl, L. H. Gade, *J. Am. Chem. Soc.* **2012**, *134*, 2946.
- [3] Review: L. H. Gade, S. Bellemin-Laponnaz, *Chem. Eur. J.* **2008**, *14*, 4142.
- [4] a) N. Schneider, M. Finger, C. Haferkemper, S. Bellemin-Laponnaz, P. Hofmann, L. H. Gade, *Angew. Chem. Int. Ed.* **2009**, *48*, 1609; b) N. Schneider, M. Finger, C. Haferkemper, S. Bellemin-Laponnaz, P. Hofmann, L. H. Gade, *Chem. Eur. J.* **2009**, *15*, 11515.
- [5] Y.-B. Kang, L. H. Gade, *J. Am. Chem. Soc.* **2011**, *133*, 3658.