Bifunctional Group 4 Metallocenes: Postcoordinative Functionalisation for Tuning Amine Borane Dehydropolymerisation Catalysts

M. Greiner[1], F. Reiß[1*], T. Holtrichter-Rößmann[2], T. Beweries[1]

[1]*Leibniz Institute for Catalysis, Albert-Einstein-Strasse 29a, 18059 Rostock, Germany*
[2]*LANXESS Organometallics GmbH, Ernst-Schering-Straße 14, 59192 Bergkamen, Germany*
[*]*fabian.reiss@catalysis.de*

The dehydrocoupling of amine boranes is an already known research field to build up polyamineboranes as a new class of materials that is analoguous to polyethylene. The hydrogen evolved during polymerisation could be used as an on-demand hydrogen source or as an *in situ* reducing reagent.[1]
Our group already investigated the structure and mechanisms of dinuclear group 4 metallocene catalysts facilitating this reaction.[2] In this contribution a new type of bifunctional catalysts with a group 4 metallocene core and a Lewis acidic or Lewis basic anchor group is introduced. A variety of these catalysts is easily accessible by the modular buildup from a precusor complex serving as a building block. The feasibility of such postcoordinative functionalisations like hydroboration is already known from litature.[3]
Volumetric measurements and NMR studies indicate that these bifunctional catalyst show a significantly increased activity compared the their unfunctionalised precursors. A possible mechanism explaining these change is *facilitated diffusion* meaning that the introcuced anchor group in second coordination sphere directs the substrate towards the active metallocene centre. This structure-activity relationship is further elucidated by computational studies.

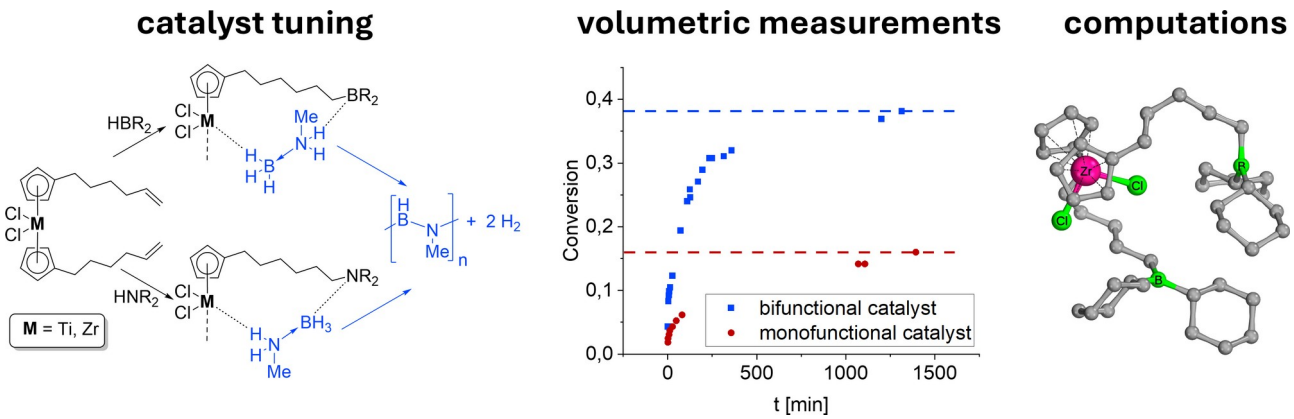

Figure 1: Modular synthetic approach for group 4 catalysts to tune the dehydrocoupling of amine boranes (left), comparison of activities of a bifunctional group 4 catalyst and its unfunctionalised precursor by volumetric detection of hydrogen generation (middle), semi-empirical approach for isomer sampling (right, xTB-crest).

Keywords: Bifunctional Catalysts, Amine Boranes, Hydrogen, Postcoordinative Functionalisation, Second coordination sphere

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References

[1] M. Rippke, X. Tian, F. Reiss, L. Wu, T. Beweries, *Chem. Eur. J.* **2025**, *31*, e202403982.
[2] K. Lindenau, N. Jannsen, M. Rippke, H. Al Hamwi, C. Selle, H.-J. Drexler, A. Spannenberg, M. Sawall, K. Neymeyr, D. Heller, F. Reiß, T. Beweries, *Catal. Sci. Technol.* **2021**, *11*, 4034-4050.
[3] a) G. Erker, R. Aul, *Chem. Ber.* **2006**, *124*, 1301-1310.
b) J. Pinkas, M. Lamač, *Coord. Chem. Rev.* **2015**, *296*, 45-90.