

Chiral Cation-Directed Hydrofunctionalization Catalysis

1st supervisor: Robert Wolf, 2nd supervisor: Hendrik Zipse

Topic:

Preliminary work in the Wolf group has been investigating (achiral) transition metalate anions and organophosphorus anions as hydrofunctionalization catalysts for alkenes, ketones and imines. This project is now studying the cation-anion interactions in such systems, which can have a significant influence on the reactivity. Ion-pairing of our catalytically active anions with chiral cations is used to develop asymmetric hydrofunctionalization reactions.

Aim of the Project:

Our recent work has shown that cobaltate and ferrate anions are potent catalysts for the hydrogenation of alkenes and imines,^{P10/1} while

phosphacyclohexadienyl anions very efficiently catalyze the hydroboration and -silylation of prochiral ketones and imines.^{P10/2}

Mechanistic investigations will serve us to gain a thorough understanding of the cation-anion interactions. Several NMR active

nuclei (¹H/¹³C/¹⁵N/¹⁹F/³¹P) can be incorporated into phosphoorganic anions as well as counteranions and substrate molecules. This will facilitate NMR studies, which are complemented by kinetic analysis and computational modelling (see also project **P7** by H. Zipse). Our major aim is to use *chiral cation-directed catalysis*²⁹ in asymmetric hydrofunctionalization reactions for the first time (Figure P10).^{164–175} Ion-pairing interactions of chiral organic cations with suitable (achiral) anionic catalysts are harnessed to achieve asymmetric induction.^{P10/1} Candidates for suitable chiral cations are C₂-symmetric ammonium and phosphonium cations, see Figure P10, and homochiral alkali metal cation-crown ether complexes. The observed enantioselectivities thus may help elucidate any catalytically relevant ion-pair formation. The formation of an intimate ion pair between the anion and the catalytically active anion is required to observe an enantioselective reaction, and enantioinduction should correlate with the strength and the specificity of the anion-cation interaction.

Within this project, PhD students will receive training in the synthesis of organic and organometallic molecules, catalytic studies, reaction monitoring by NMR and IR spectroscopy, kinetic studies, reaction time profile analysis and modelling of mechanistic steps by quantum chemical calculations.

Connections within the RTG: R. M. Gschwind (NMR of ion pairs), H. Zipse (calculations and chiral organic cations), B. König and O. Reiser (chiral organic cations and crown ethers), J. Bauer und N. Korber (transition metalate anions).

- P10/ 1)** a) P. Büschelberger, D. Gärtner, E. Reyes-Rodriguez, F. Kreyenschmidt, K. Koszinowski, A. Jacobi von Wangelin, R. Wolf, *Chem. Eur. J.* **2017**, *23*, 3139–3151.
 b) T. M. Maier, S. Sandl, I. G. Shenderovich, A. Jacobi von Wangelin, J. J. Weigand, R. Wolf, *Chem. Eur. J.* **2019**, *25*, 238–245.
P10/ 2) M. Margeson, M.Sc. Thesis, Universität Regensburg, 03/2019 and unpublished results.

