Smart Phosphorus Ligands for Cooperative Homogeneous Catalysis: *Challenges and Chances*

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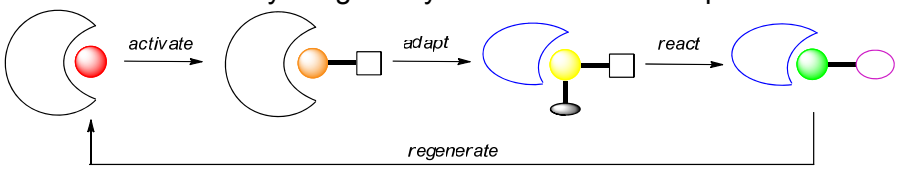
Cooperative catalysis, which involves participating ligand fragments, is a ubiquitous concept in the chemistry of biological systems, wherein the protein scaffold or cofactors around the active site actively facilitate substrate turnover. In contrast to the (bioinspired) application of multimetallic cooperative systems for selective transformations, the design of smart, responsive or adaptive ligand systems for applications in cooperative homogeneous catalysis is only slowly gaining momentum. Major challenges include asymmetric induction as well as the use of earth-abundant metals, next to the preparation of privileged systems that can accommodate various reaction conditions and facilitate different mechanisms. For many applications, in particular those that concern late-transition-metal systems, phosphorus-based ligands have made a huge impact on the progress of homogeneous catalysis. It is therefore logical to extend this chemistry to ligand systems that show cooperative characteristics.



We will demonstrate ongoing research in the area of redox non-innocent ligands and metalloradicals, proton-transfer systems[2] and hybrid versions thereof, also with relation to the reactivity of first-row transition metal species, and preliminary results in *inter alia* the hydroamination of alkenes. Also physical-chemical studies on these non-innocent systems will be included. Furthermore, recent results on the chemistry and application of responsive pseudo-pincer systems will be discussed.[4] Novel hybrid tridentate ligands and their metal complexes (Rh, Ir) will be disclosed, aiming for enhanced adaptability toward unactivated substrates and small molecules.[5]

References:

[1] J.I. van der Vlugt, J.N.H. Reek, *Angew. Chem. Int. Ed.* **2009**, *48*, 8832.

[2] a) J. Wassenaar, B. de Bruin, M.A. Siegler, A.L. Spek, J.N.H. Reek, J.I. van der Vlugt, *Chem. Commun.* **2010**, *46*, 1332; b) J. Wassenaar, M.A. Siegler, B. de Bruin, A.L. Spek, J.N.H. Reek, J.I. van der Vlugt, *Inorg. Chem.* **2010**, *in press*.

[3] a) J.I. van der Vlugt, E.A. Pidko, D. Vogt, M. Lutz, A.L. Spek, *Inorg. Chem.* **2009**, *48*, 7513; b) J.I. van der Vlugt, M.A. Siegler, M. Janssen, D. Vogt, A.L. Spek, *Organometallics* **2009**, *28*, 7025; c) J.I. van der Vlugt, M. Lutz, E.A. Pidko, D. Vogt, A.L. Spek, *Dalton Trans.* **2009**, 1016; d) J.I. van der Vlugt, E.A. Pidko, D. Vogt, M. Lutz, A.L. Spek, A. Meetsma, *Inorg. Chem.* **2008**, *47*, 4442.

[4] R. Lindner, B. van den Bosch, J.N.H. Reek, J.I. van der Vlugt, *submitted for publication*.

[5] J.I. van der Vlugt, *Chem. Soc. Rev.* **2010**, *in press.*