

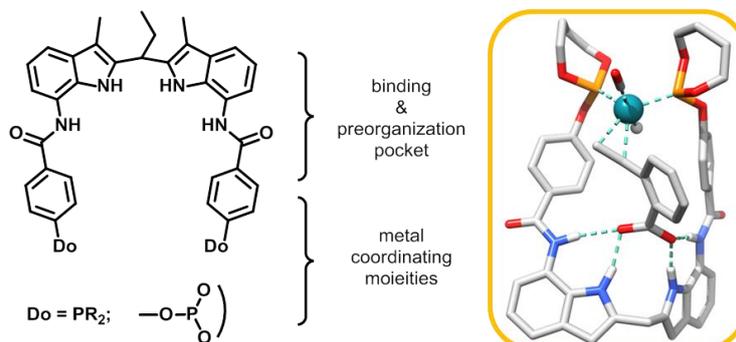
Supramolecular control of selectivity in transition metal catalysis using ligands functionalized with an anion binding pocket

Paweł Dydio and Joost N. H. Reek

*van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands;
p.f.dydio@uva.nl*

The selectivity displayed by transition metal catalysts is one of the key elements in catalysis, and various tools to control this by ligand modification have been reported. Some selectivity issues are, however, difficult to solve using the traditional methods. Therefore we have an interest in the development of new approaches using supramolecular chemistry, guided by the lessons that we can learn from Nature.¹

Here we present DIMPhos, a new class of bidentate phosphorus ligands equipped with an integral anion binding site.² The supramolecular interactions between the binding pocket of the Rh(DIMPhos)-catalysts and substrates containing anionic functionalities provide an excellent design concept to achieve remote control of the regioselectivity in hydroformylation by substrate pre-organization.³ The carefully designed ligand-substrate interactions allow for an unprecedented full reversal of selectivity to otherwise unfavorable products, thus opening up novel pathways in chemical synthesis.⁴



Further, the pocket of the Rh(DIMPhos)-catalysts can also be used for catalyst tuning by binding small cofactors – anions of chiral acids – allowing for supramolecular modulation of the enantioselectivity of the catalyst. This strategy afforded excellent enantioselectivities (ee's up to 99%) for the hydrogenation of several different olefins, demonstrating its potential.⁵

In this contribution we discuss the mechanism and the substrate range of this multifunctional catalytic system both in terms of controlling selectivity by substrate pre-organisation and catalyst tuning by cofactor binding.

1. J. N. H. Reek *et al.*, *Nature Chem.* **2010**, 2, 615; *Chem. Soc. Rev.* **2008**, 37, 247.
2. P. Dydio, D. Lichosyt, T. Zieliński, J. Jurczak: *Chem. Commun.* **2009**, 45, 4560; *Org. Lett.* **2010**, 12, 1076; *Chem. Eur. J.* **2012**, 18, 13686.
3. P. Dydio, W.I. Dzik, M. Lutz, B. de Bruin, J. N. H. Reek, *Angew. Chem. Int. Ed.* **2011**, 50, 396.
4. P. Dydio, J. N. H. Reek, *Angew. Chem. Int. Ed.* **2013**, DOI: 10.1002/anie.201209582 (Highlighted in *Nature Chem.* **2013**, 5, 250).
5. P. Dydio, C. Rubay, T. Gadzikwa, M. Lutz, J. N. H. Reek, *J. Am. Chem. Soc.* **2011**, 133, 17176.