

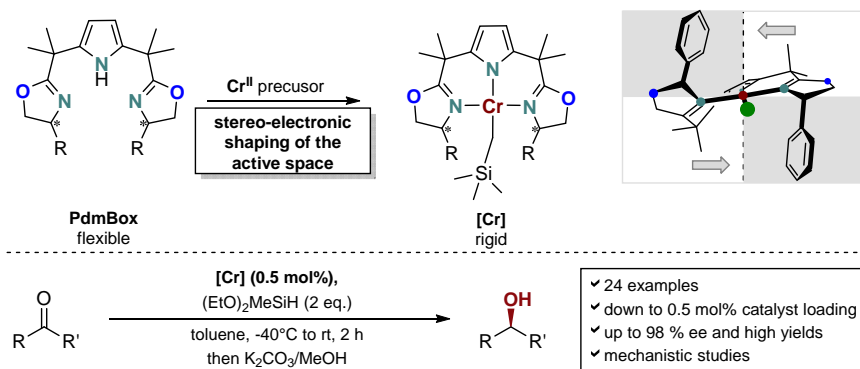
HIGHLY ENANTIOSELECTIVE CHROMIUM(II) PINCER CATALYZED HYDROSILYLATION OF KETONES

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Costs, toxicity and low abundance of noble metal catalysts has led to the development of a non – conjugated, rigid and planar *N,N,N* pincer-type ligand in combination with chromium in the formal M^{II} oxidation state furnishing a catalytic system of unprecedented activity and selectivity[1].



A unique square planar, chiral chromium(II) alkyl complex was found to serve as a potent precatalyst for the reduction of a broad range of aryl-alkyl and dialkyl ketone derivatives. Bis(oxazolinyl)dimethylmethylpyrrol (PdmBox) as stereo directing ligands provided the key to the chromium(II)-catalyzed highly enantioselective hydroxylation of ketones. The electronic preference of the open d^4 shell of chromium(II) to form square planar complexes firmly locks the molecular catalyst in a set geometry giving rise to two blocked quadrants of the coordination sphere. The well-defined precatalyst was fully characterized (*EA*, *MS*, paramagnetic *NMR* and magnetic moment in solution). Additionally, X-ray crystal structure analysis revealed the coordination geometry around the chromium center, which is best described by a slightly distorted square-planar arrangement. This earth abundant base metal catalytic platform produces the corresponding chiral alcohols in excellent isolated yields with up to 98 % *ee* under mild reaction conditions (–40 °C to rt) and at low catalyst loadings (as low as 0.5 mol%). A series of control experiments (e.g. radical traps, *KIE*, Hammett analysis) were carried out in order to identify the nature of the elementary steps and the rate-determining kinetics. A direct hydride transfer reaction mechanism is proposed.

[1] C. Schiwiek, V. Vasilenko, H. Wadepohl, Lutz H. Gade, *Chem. Commun.* **2018**, 54, 9139-9142.