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(oxazolinyldimethylmethyl)pyrrol (PdmBox) as stereo directing ligands provided the key to the chromium(II)-catalyzed highly enantioselective hydrosilylation 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 (E.A, 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 and high yields. A series of control experiments (e.g. radical traps, KIE, Hammet 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.