16b Asymmetric Hydrosilylation of Imines Using a Chiral Ansa-Titanocene Catalyst: Mechanistic Studies and Reaction Kinetics

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Chiral *ansa*-ethylene-bis(tetrahydroindenyl) titanium complexes, EBTHI-TiX_2, first introduced by Brintzinger [1], are highly active and selective catalysts for enantioselective reactions (e.g. hydrogenations of olefins, ketones and imines, as well as various polymerization reactions). We aim to show the use of a homogeneous chiral titanocene catalyst for the asymmetric reduction of imines to prepare chiral amines, which are important intermediates in the pharmaceutical and fine chemicals industry. Specifically, our research concentrates on the hydrosilylation of 2-phenylpyrroline using (R,R)-ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)titanium (R)-1,1'-binaphth-2-olate (1) as a precatalyst. After activation with n-BuLi and phenylsilane this catalytic system has proven to be very practical in the preparation of chiral amines with high yields (>98%) and enantioselectivity (75% ee). The investigation of the reaction kinetics has revealed a strong dependence on reaction temperature and reactant concentration. While there is a general consensus that the key intermediate in titanocene catalyzed hydrosilylations is a Ti(III)-H intermediate [2,3], we propose this catalyst procedures through a Ti(IV)-H intermediate. In summary, our results clearly demonstrate that the hydrosilylation of imines with the chiral catalyst (1) offers a very convenient and safe method for the preparation of enantiomerically pure amines. Further optimization of the metallocene-catalyzed reaction can lead to more attractive catalytic complexes. References: [1] F.R.W.P Wild., J. Zsolnai, G. Huttner, H. H Brintzinger, J. Organomet. Chem., 1982, 232, 233 [2] X. Verdagauer, U.E.W. Lange, S.L. Buchwald, Angew. Chem. Int. Ed., 1998, 37, 1103 [3] K. Rahimian, J.F. Harrod, Inorg. Chim. Acta, 1998, 270, 330