Abstract

This thesis focuses on a detailed study on the activity of manganese guanidine complexes in the epoxidation of olefinic substrates. In this context, 18 new polyfunctional guanidine ligands were synthesised and the influence of ligand substitution on catalytic activity and selectivity was analysed. Moreover, 16 new mono- and polynuclear manganese and iron complexes with the guanidine-quinoline ligands DMEGqu, TMGqu and TEGqu were synthesised and structurally characterised which allow for new insights into the coordination potential of these ligands.

At first, the epoxidation conditions were optimised with regard to oxidation reagent, solvent, manganese source and catalyst loading. Peracetic acid was identified as most efficient oxidation reagent. Then, the ligands were systematically screened towards the structural influences on the epoxidation of 1-octene: for this purpose the denticity, the bite, the guanidine function as well as the amine function were varied. For the selected DMEGepy/Mn(CH₃COO)₂ system, the substrate spectrum was extended to a series of chemically interesting olefins with different electronic demands. In the next step, the kinetics of the epoxidations with the DMEGepy/Mn(CH₃COO)₂ system were studied in detail: the reactions rate has a first order dependence on the oxidant and the reaction order is 0.5 in terms of catalyst concentration, but it is independent of the substrate concentration. First investigations on the reaction mechanism by means of EPR spectroscopy, ESI/MS spectrometry and UV/Vis spectroscopy lead to a hypothetic model of a polynuclear higher valent active species.

With the present thesis, the polyfunctional guanidine ligands prove to stabilise efficiently manganese complexes which are capable to epoxidise olefins under oxidative and even acidic conditions. This study might serve as starting point for further investigations. Hence, this ligand class of strong neutral N-donors has opened up a new application in an industrially relevant field.