

SUMMARY OF Ph.D. DISSERTATION

School Fundamental Science and Technology	Student Identification Number	SURNAME, First name SATO, Mitsuo
Title Stereoselective Synthetic Organic Reactions Catalyzed by Cobalt and Manganese Complexes		
Abstract <p>The highly enantioselective cyclopropanation of styrene derivatives and diazoacetates was effectively catalyzed by rationally designed β-ketoiminato cobalt(II) complexes, whose ligands were prepared from optically active 1,2-diarylethylenediamine and 3-oxobutanoates. The addition of a catalytic amount of <i>N</i>-methylimidazole significantly accelerated the reaction and also improved the enantioselectivity. During the examination of the reaction solvents, methanol was found to be a suitable solvent for the present reaction. The rate of enantioselectivity was remarkably improved in methanol. The superiority of methanol to THF with the <i>N</i>-methylimidazole system was observed for the cyclopropanation of the 1,1-disubstituted ethylenes. By using methanol as the solvent, the 1,1-disubstituted ethylenes were smoothly converted to their corresponding products with high yield and high enantiomeric excesses. This procedure has possibilities to provide the highly enantioselective cyclopropanation as an environmentally benign system.</p> <p>The efficient preparation of optically pure cyclic C_2-amines has been established using the enantioselective borohydride reduction catalyzed by β-ketoiminato cobalt(II) complex. Thus obtained optically pure cyclic amine was employed as the chiral auxiliary for aerobic oxidation of α,β-unsaturated carboxamide with the combined use of phenylsilane and tris(dipivaloylmethanato)manganese(III) complex catalyst to afford the corresponding α-hydroxycarboxamide in high yield with high stereoselectivity. It was assumed that the carbanion equivalent was generated from α,β-unsaturated compounds with tris(dipivaloylmethanato)manganese(III) complex and phenylsilane. Then the di-<i>tert</i>-butylazodicarboxylate was employed as an electrophile for the α,β-unsaturated carboxylate containing camphorsultam as the chiral auxiliary to afford the corresponding α-hydradinocarboxylate in high yield with high stereoselectivity.</p>		