

Abstract

A series of chiral phosphinoferrocene amides was prepared by the condensation either of 1'-((diphenylphosphino)ferrocene-1-carboxylic acid (Hdpf) or its planar-chiral 1,2-isomers and amino acid methyl esters in the presence of peptide coupling agents. The resulting phosphinoamides were tested as ligands in Cu-catalyzed asymmetric conjugate additions of diethylzinc to chalcones and in Pd-mediated asymmetric allylic substitution reactions of 1,3-diphenylallyl acetate with the respective nucleophile (alkylation, amination and etherification). The catalytic tests were focused on an optimization of the reaction parameters (solvent, temperature, base, metal/ligand ratio) and on survey of various substrates. Compounds based on Hdpf proved to be better ligands in both catalytic reactions than their planar chiral analogues. In order to rationalize the influence of the ligand structure on the reaction course and also to interpret the catalytic results, several model complexes were prepared and structurally characterized.

Other three series of non-chiral complexes were prepared from the corresponding (η^6 -arene)ruthenium(II) precursor and Hdpf-glycine conjugates; the neutral complexes of the type [(arene)RuCl₂(Hdpf-Gly(R)- κP)] (arene = benzene, *p*-cymene, hexamethyl-benzene; R = OMe, NH₂, OH) as well as two series of mono- and dicationic complexes resulting from the substitution of the Ru-bound chloro ligands by acetonitrile, which were isolated as [PF₆]⁻ salts. These complexes proved to be highly active pre-catalyst for oxidation of secondary alcohols to the corresponding ketones with *t*-BuOOH in water.

Finally, a new type of ferrocene-based amino acid conjugate, 2-[(methoxycarbonyl)methyl]-2-aza[3]ferrocenophane, was designed and obtained by the condensation reaction of 1,1'-bis(hydroxymethyl)ferrocene and glycine methyl ester. The aza[3]ferrocenophane was subsequently reacted with 2,4,6-trinitrophenol to afford the corresponding picrate.

All newly prepared compounds were fully characterized by multinuclear NMR, MS and IR spectroscopy, elemental analysis and the crystal structures of several representatives were determined by X-ray crystallography. In addition, electrochemical properties of the mentioned ruthenium complexes and the aza[3]ferrocenophane were studied by cyclic voltammetry.