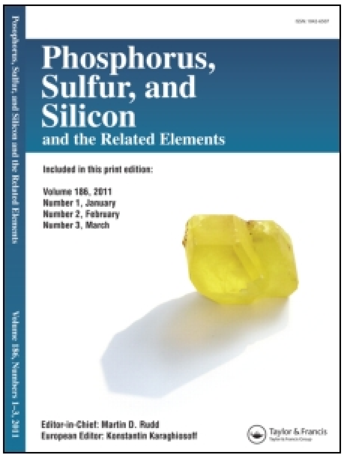

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Design and Synthesis of Optically Active Trans-Chelating Diphosphine Ligands. Application for Catalytic Asymmetric Synthesis

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New chiral diphosphines 2,2"-bis[1-(disubstituted phosphino)ethyl]-1,1"-biferrocene, having both central and planar elements of chirality, was designed for a trans-chelating chiral diphosphine ligand (TRAP) for transition metals and synthesized form optically active N,N-dimethyl-1-ferrocenyl ethylamine. Some transition-metal complexes with the TRAP ligands were prepared and utilized as a chiral catalyst for asymmetric synthetic reactions.

Keywords: trans-chelating chiral diphosphines; catalytic asymmetric synthesis

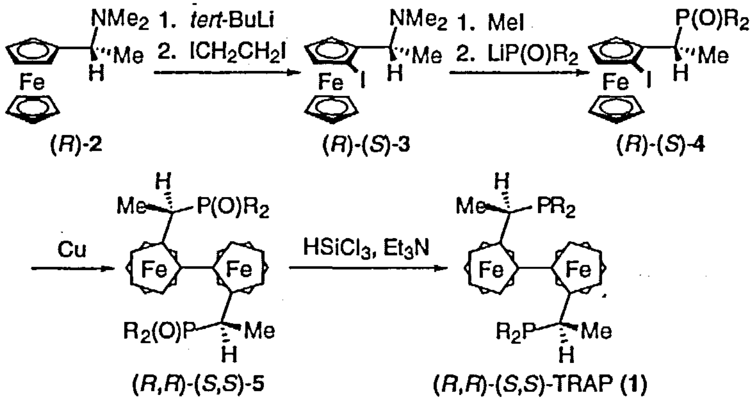
INTRODUCTION

Catalytic asymmetric synthesis with chiral transition metal complexes has been recent topics of organic synthetic chemistry. A variety of optically active phosphines have so far been designed and synthesized for chiral ligands on transition metal complexes. Especially, chiral diphosphine ligands, which have found wide applications for asymmetric synthesis, coordinate to metal in cis-chelating manner and create chiral environment around the metal center by sterically rigid and bulky substituents on the each phosphine atoms. Recently, we have developed a new type of chiral diphosphine ligands TRAPs, (R,R)-(S,S)- and (S,S)-(R,R)-2,2"-bis[1-(diaryl- or dialkylphosphino)ethyl]-1,1"-biferrocenes, which were designed for trans-chelation coordination on transition metals unlike the conventional cis-chelating diphosphines. TRAPs on transition metal have been demonstrated to be effective chiral ligands for some catalytic enantioselective reactions.

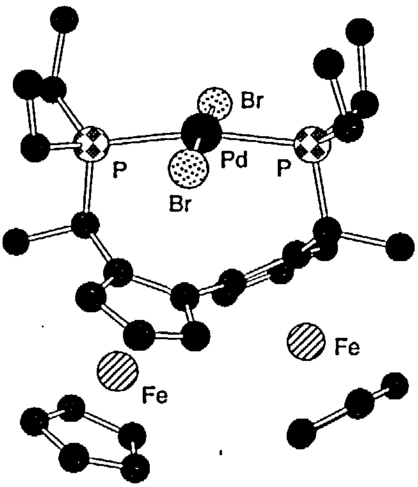
Synthesis of TRAP Ligands and Transition Metal Complexation[1,2]
Trans-chelating chiral diphosphine ligands (R,R)-(S,S)-aryl- and alkyl TRAPs (**1**) were synthesized according to the Scheme 1, starting form optically pure (R)-N,N-dimethyl-1-ferrocenylethylamine (**2**), which was obtained by optical resolution of its racemate with tartaric acid. For introducing diarylphosphinyl group on the side chain, the dimethylamino group of (R)-(S)-**3** was substituted by lithium diphenylphosphinite in acetonitrile with complete retention of configuration. However, the same procedure was not successfully applicable for introduction of dialkylphosphinyl group. Dialkylphosphinyl group on the ferrocene side chain was stereoselectively introduced by treatment of (R)-(S)-**3** with excess of acetic anhydride followed by substitution reaction with dialkylphosphines in acetic acid. The diaryl and dialkylphosphines thus prepared were not stable enough to be handled in the air. Therefore, they are converted to the corresponding phosphine oxide (R)-(S)-**4** by oxidation with hydrogen peroxide for the experimental convenience. The Ullmann coupling of (R)-(S)-**4** at 130°C for 12 h was achieved with activated copper powder, producing C_2-symmetric biferocene (R,R)-(S,S)-**5**, which was purified by column chromatography on silica gel. Finally, deoxygenation of **5** was carried out by treatment of

trichlorosilane in the presence of triethylamine to give TRAPs (**1**) in about 40% overall yield.

Scheme 1



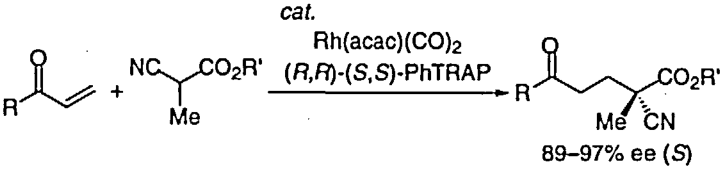
Transition-metal complexes [Pd(II), Pt(II), Ir(I), Rh(I)] with trans-chelating chiral diphosphine TRAPs thus synthesized were formed and characterized by X-ray analysis as well as NMR spectroscopy.



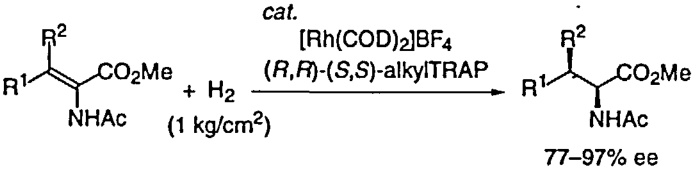
X-ray Crystal Structure of Pd(II)Br_2(EtTRAP)

Synthetic usefulness of Rh(I)TRAP complexes is exemplified as follows.

Asymmetric Michael reaction of 2-cyanopropionates with vinyl ketones or acrolein in the presence of 0.1–1 mol% of a Rhodium / PhTRAP complex, which is prepared in situ by mixing Rh(acac)(CO)2 and (R,R)-(S,S)-PhTRAP, gave optically active Michael adducts with high enantiomeric excesses (89–97% ee) in high yields.[3]



Asymmetric hydrogenation of β,β-disubstituted α-acetamidoacrylates was achieved in high enantioselectivities (77–97%ee) by Rhodium / alkylTRAP complex.[4]



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