Towards a new class of P-trifluoromethylated BINAP-derived ligands

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Introduction

The advent of binaphthyl ligands in asymmetric catalysis has induced the development of an array of diversely functionalized ligands containing the binaphthyl backbone. 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), 1, the original precursor of phosphine-based binaphthyl ligands, was first discovered by Noyori and co-workers in 1980. Its synthesis has been optimized, and since then many modifications inducing sterical and electronic effects have been introduced. Examples such as perfluorinated BINAP 2 or sulfonate derivative 3 allow carrying out asymmetric syntheses in aqueous or supercritical medium and giving high enantioselectivities.

Fig. 1. BINAP and BINAP derivatives

The diversity and relative ease of access makes it one of the few ligands not only produced but also used on industrial scale, e.g. for the synthesis of menthol.

Fig. 2. Key asymmetric transformation in the Takasago menthol synthesis

One focus of the Togni group research is to synthesize and develop new ligands incorporating a trifluoromethyl moiety. CF₃-substituents introduce little steric bulk and have interesting electron-withdrawing properties, which allow specific tuning of ligands for desired outcome in enantioselective transformations.

P-trifluoromethylation

Electrophilic trifluoromethylation reagents based on a hypervalent iodine scaffold developed in our group have been successfully applied to the synthesis of mono- or bistrifluoromethylated phosphines.

Fig. 3. Trifluoromethylation of phosphines using hypervalent iodine reagents

Ligand development

The synthesis of a P-trifluoromethylated BINAP ligand 6 was initially achieved in our group in five steps from (R)-BINOL₅.

Fig. 4. Synthetic pathway towards the first bistri fluoromethylated BINAP ligand

The coordination properties of this first representative of a new class of BINAP ligands was determined by X-ray diffraction of palladium(II) complex 7.

Fig. 5. X-ray structure bis(CF₃)-BINAP-Pd complex 7

Similar features were observed with standard BINAP complexes reported in literature, such as bite angle (92.906°) and dihedral angle (73.67°).

Ongoing research and outlook

Part of our research is currently focused on the expansion of this novel class of ligands by preparing various derivatives, monodentate as well as bidentate, bearing one or more trifluoromethyl substituents. Their potential will be assessed in standard asymmetric homogeneous catalysis.

Fig. 6. Synthetic route towards P-trifluoromethylated ligands

Further efforts will also be turned towards ligand synthesis with modified backbones and their activity will be assessed in asymmetric catalysis and compared to the BINAP-derived ligands.

References


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Further Information

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