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Iridium complexes with P-stereogenic phosphino imidazole ligands: Synthesis, structure and catalysis

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Dedicated to Steve Buchwald for his inspiring contributions to the field of organometallic catalysis.

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ABSTRACT

The synthesis of optically and diastereomerically pure P-stereogenic phosphine-imidazole ligands is reported. The new ligands contain either a benzoimidazole or a 4-phenylimidazole as a *N*-donor fragment. The ligands have been coordinated to iridium and the structure of the corresponding cationic COD complexes has been determined by X-ray analysis. The combination of the chiral phosphorus atom and the imidazole substituents generate a strong chiral environment around the metal center. Preliminary hydrogenation reactions with a model cyclic β-enamide are also reported.

1. Introduction

The use of P-stereogenic ligands (P*) is as old as organometallic asymmetric catalysis [1]. Although at some point this family of ligands fell from favor, in the last decades a number of research groups have developed new type of P*-ligands which may be recognized among the most effective ligands in the chemist toolbox [2–4]. Since 2010, our group has developed different P-stereogenic synthons that can be conveniently used to assemble P-P, P-O and P-N ligands [5–7]. Among these synthons, we have recently reported the synthesis of optically pure *tert*-butylmethylphosphinous acid borane **1,** which we used in the synthesis of P-stereogenic phosphino-oxazoline MaxPHOX family of ligands (Fig. 1). MaxPHOX ligands have provided excellent results in the Ir-catalyzed asymmetric isomerization and hydrogenation reactions [8–12]. P,*N*-Iridium complexes with imidazole as heterocyclic *N*-donor group have been reported in the literature, however, to our knowledge none of these contain a P-stereogenic phosphine [13,14]. In this work we report on the synthesis, coordination and X-ray structures of phosphine-imidazole ligands derived from phosphinous acid **1** and valine. Preliminary asymmetric hydrogenation reactions of a model cyclic β-enamide are also reported.

2. Results and discussion

2.1. Ligand synthesis

Phosphino imidazole ligands have been synthetized according to the retrosynthetic analysis shown in Scheme 1. Condensation of

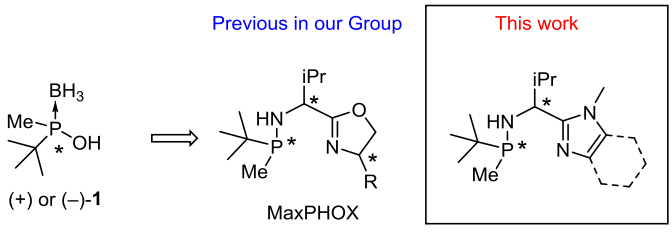

Fig. 1. General structure of the ligands.

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