Journal of Organometallic Chemistry 717 (2012) 135–140

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Neutral *vs.* cationic rhodium (I) complexes of bulky *N*-phosphino sulfinamide ligands: Coordination modes and its influence in the asymmetric hydrogenation of *Z*-MAC

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ARTICLE INFO

Article history:
Received 8 May 2012
Received in revised form
28 June 2012
Accepted 8 July 2012

Keywords:
P,S and P,O ligands
Rhodium
Asymmetric hydrogenation
Sulfinamides

ABSTRACT

Here we report the synthesis of a new *N*-di-*tert*-butylphosphino-*tert*-butylsulfinamide (PNSO) ligand and its corresponding *p*-tolylsulfinamide analog. The coordination of these compounds to rhodium to form a neutral and apolar complex is described, followed by the subsequent protonation of said complexes to quantitively form the more orthodox, cationic rhodium species containing a tetrafluoroboric counterion. The crystallographic structure of the *tert*-butylsulfinamide-derived cationic species was obtained and is elucidated. It outlines coordination from the sulfinamide group to the rhodium atom and shows no preference between O- and S-coordination as both complexes can be seen in one unit cell of the crystal. The efficacies of the neutral species and the salt species were tested in the asymmetric hydrogenation of methyl (Z)-α-acetamido cinnamate (*Z*-MAC). The *p*-tolylsulfinamide-derived complexes gave no hydrogenation while the *tert*-butylsulfinamide-derived ones produced hydrogenation with complete conversion but low enantioselectivities. The stereochemical outcome of the reaction was analyzed by means of the quadrant method.

1. Introduction

Chiral bi-dentate ligands have become highly relevant in the field of asymmetric catalysis. These compounds not only increase reactivity but more importantly, they induce the high enantioselectivities currently demanded by the pharmaceutical industry [1]. Thus moving the chiral information of the ligand as close as possible to the catalyzing metal center would be the best way to efficiently confer chirality to and increase enantioselectivities of the catalytic transformations that the catalyst is mediating. This could be achieved by conferring chirality to the metal-coordinating atom. P-stereogenic bidentate diphosphine ligands are extremely proficient in asymmetric transformations [2]. In 2004 Hoge et al. reported the synthesis and efficacy of the three-hindered quadrant chiral ligand trichickenfootphos (TCFP) in the Rh-catalyzed asymmetric hydrogenations of α- and β-acetamido dehydroamino acid substrates [3]. The excellent enantioselectivities obtained suggested the C_1-symmetric, 3-hindered quadrant chiral ligand design was an excellent template to follow. MaxPHOS, an analog of the TCFP ligand, was developed in our laboratory and was first reported in 2010 [4,5]. As with TCFP, it showed excellent enantioselectivity in the asymmetric hydrogenation of α- and β-acetamido dehydroamino acid substrates. Despite the great efficiency of this type of ligand, its synthesis remains somewhat laborious [6]. In this respect, here we addressed the preparation of other cost-effective 3-hindered quadrant ligands that can be readily assembled from commercially available materials (Fig. 1).

We previously showed that the PNSO family of ligands, those containing a sulfinamide moiety bound to a phosphine group through the nitrogen atom where chirality resides on sulfur, can be highly efficient when applied to the intermolecular asymmetric Pauson–Khand reaction [7]. These ligands can be obtained in a very straightforward manner, often involving a one-step, one-pot synthesis using chiral sulfinamides that are commercially available in large amounts [8]. Also, we demonstrated that ligands such as **1** and similar analogs coordinate readily to rhodium and other metals to give either P,O or P,S bidentate coordination [9]. The positive results with these ligands in the Pauson–Khand reaction led us to test their efficacy in rhodium-catalyzed asymmetric hydrogenation of dehydroamino acids. We were willing to test whether the *N*-di-*tert*-butylphosphino-*tert*-butylsulfinamide ligand (PNSO) (**2**) could be another example of the 3-hindered quadrant chiral ligand

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http://dx.doi.org/10.1016/j.jorganchem.2012.07.008