

Synthesis of Chiral Thiazoline Ligands Tethered to a Sulfur Function and First Immobilization of a Thiazoline-Ligand

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ABSTRACT: A new family of thiazoline ligands tethered to a sulfanyl or a sulfinyl group has been prepared using short and efficient reaction sequences. Among the different structures, one sulfanyl-thiazoline homopolymer was synthesized as a first example of an immobilized thiazoline ligand. The catalytic properties of these new ligands were evaluated in the Pd-catalyzed allylic substitution. © 2010 Wiley Periodicals, Inc. Heteroatom Chem 21:242–249, 2010; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20603

INTRODUCTION

Compared with the widely used nitrogen and phosphorus-containing chiral ligands in asymmetric metal-catalyzed reactions, the sulfur counterparts have been less studied for this purpose. However, in recent years, the number of studies dealing with the chiral sulfur-containing ligands has increased con-

siderably leading to the publication of some reviews [1].

Among the large variety of chiral ligands, the thiazolines, which are sulfur-analogues of oxazolines, represent a young family of ligands [2]. They have proved to be useful sulfur-containing ligands in various metal-catalyzed reactions and to behave sometimes differently from oxazolines. Among the various structures of thiazoline-ligands including bis(thiazolines) [3a–f], phosphine-thiazolines [3d,e], pyridyl-thiazolines [3d–f], oxazoline-thiazolines [3g,l], ferrocenyl-bis(thiazolines) [3h], hydroxyalkyl-thiazolines [3j], and tris(thiazolines) [3k], only one example of sulfanyl-thiazoline ligand has been described [3i]. These ligands are of interest because they contain one S-coordinating and one S-noncoordinating atom [1a].

This paper describes the preparation of a series of sulfanyl- and sulfinyl-thiazolines, and the first example of the immobilization of a thiazoline ligand. The catalytic properties of these new ligands have been evaluated in the well-known reaction test, the Pd-catalyzed allylic substitution, and the results are reported herein.

RESULTS AND DISCUSSION

Four types of structures have been selected for this study (Fig. 1). Some of them can be considered as the sulfur analogues of sulfanyl-oxazoline *N*, *S*-ligands described by Williams [4]. Ligands of type **I** and **II** are thiazolines bearing, respectively, a sulfanyl or a

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