Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 1048–1057
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

# Synthesis and characterization of new chiral palladium β-diimine complexes

Doris Domin [a], David Benito-Garagorri [a], Kurt Mereiter [b], Christian Hametner [a], Johannes Fröhlich [a,*], Karl Kirchner [a,*]

[a] *Institute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria*
[b] *Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9, A-1060 Vienna, Austria*

Received 14 September 2006; received in revised form 21 October 2006; accepted 31 October 2006
Available online 7 November 2006

Dedicated to Professor Miha Tišler, Professor Emeritus of the University of Ljubljana, on the occasion of his 80th birthday.

## Abstract

The synthesis and characterization of a range of chiral β-diimine ligands and their complexes with palladium(II) has been investigated. The introduction of chirality can be easily achieved through a combination of both achiral and chiral building blocks. The absolute configuration of the stereochemical centers has been determined. In addition, representative X-ray structures of both ligands and complexes have been determined.

*Keywords:* β-Diimines; Chiral ligands; Palladium(II); Square-planar complexes

## 1. Introduction

Nickel and palladium complexes containing sterically demanding α-diimine (diazabutadiene) ligands are highly efficient catalysts for olefin polymerizations [1–3], alkyne cyclotrimerizations [4] and, as shown recently, also for Suzuki cross-coupling reactions [5]. On the other hand, few investigations have focused on the chemistry of analogous nickel and palladium β-diimine complexes. Feldman et al. reported the synthesis of a sterically hindered β-diimine ligand bearing no substituents at the $C_\beta$ atom and examined its reactions with Ni(II) and Pd(II) catalyst precursors [6]. However, β-diimines lacking substituents at the central carbon atom typically form hydrogen-bridged β-iminoamine tautomers. Accordingly, in the presence of base, e.g., under catalytic conditions, deprotonation occurs giving rise to the formation of β-diketiminate complexes [7] and other products [8] rather than β-diimine complexes. Recently, Woods and co-workers synthesized several β-diimine ligands in which the problematic CH acidity was circumvented by diimine dialkylation [9]. In a subsequent paper, these authors described the synthesis of some palladium β-diimine complexes and provided structural comparisons with the corresponding α-diimine analogues [10]. We recently reported the synthesis and reactivity of a series of sterically demanding non-chiral β-diimine ligands as well as their Ni(II) and Pd(II) complexes, where the central carbon atoms of the ligands were part of five- and six-membered rings in order to ensure that the ligands kept their diimine character even under basic conditions [11].

In the present contribution we extend our synthetic efforts to obtain novel chiral β-diimine ligands, where chirality can be introduced into two different positions of the ligands by using a combination of chiral and achiral building blocks. Condensation of an achiral dialdehyde with chiral amines renders the ligands chiral at the diimine moieties, whereas a chiral dialdehyde and an achiral amine

---

[*] Corresponding authors. Fax.: +43 1 58801 15341; fax: +43 1 58801 15499 (K. Kirchner).

*E-mail addresses:* jfroehli@ioc.tuwien.ac.at (J. Fröhlich), kkirch@mail.zserv.tuwien.ac.at (K. Kirchner).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.10.064

leaves the ligand backbone chiral. A combination of these possibilities finally affords ligands which are chiral both at the ligand backbone and at the diimine functionality. Moreover, the synthesis of a series of Pd(II) complexes with our new ligands is described. Representative X-ray structures of ligands and palladium complexes are reported.

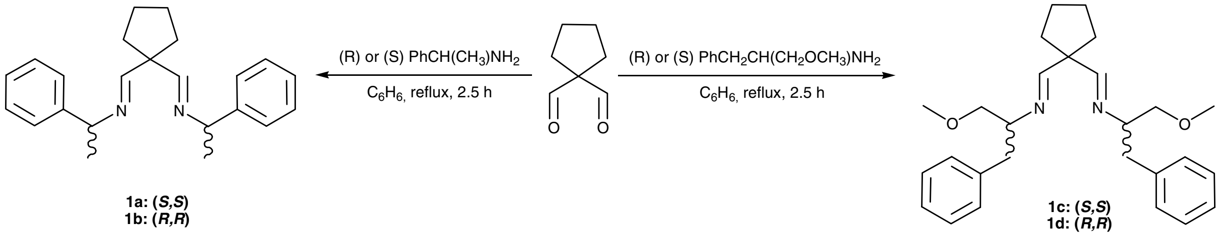
## 2. Results and discussion

### 2.1. Synthesis of the ligands

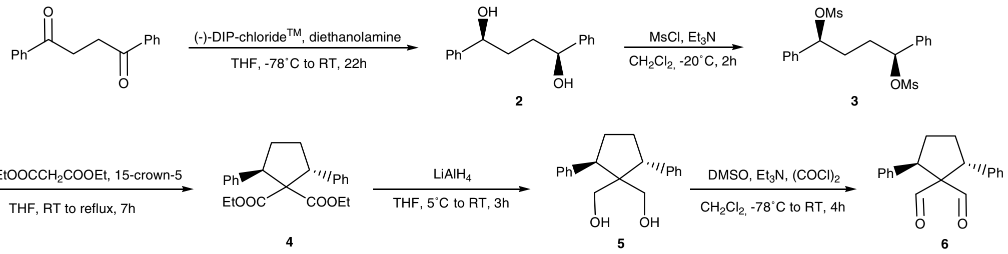
Following the methodology established previously [11] the β-diimine ligands were synthesized by condensation of 1,1-cyclopentanedicarbaldehyde and various amines. By using chiral amines diimines bearing chirality at the diimine moiety were obtained (Scheme 1).

To introduce chirality into the cyclic framework, the synthesis of a chiral dialdehyde was necessary (Scheme 2). After asymmetric reduction of 1,4-diphenylbutane-1,4-dione using commercially available (−)-DIP-chloride the resulting diol (*S*,*S*)-**2** was converted into the dimesylate (*S*,*S*)-**3** using an optimized procedure [12]. The cyclization step was carried out by alkylation with malonic acid diethylester and sodium hydride in the presence of 15-Crown-5 to yield the enantiomerically pure diethyl malonate (*R*,*R*)-**4**. Traces of (*meso*)-diester were easily removed by column chromatography.

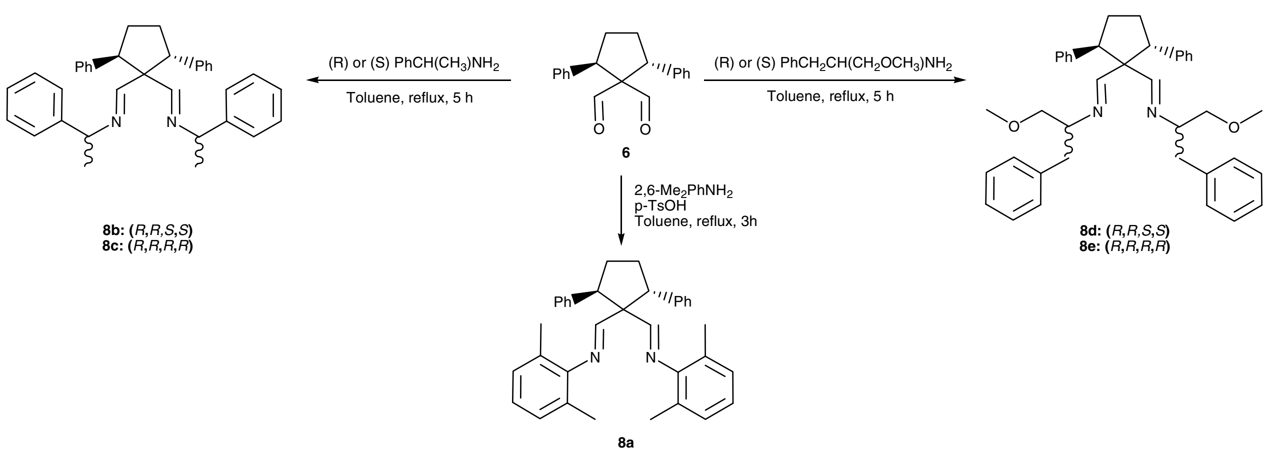
Reduction with lithium aluminum hydride to the diol (*R*,*R*)-**5** followed by a Swern oxidation gave the dialdehyde (*R*,*R*)-**6** in an excellent yield. The enantiomeric excess was estimated by synthesis of the racemic diol (*rac*)-**5** and (*meso*)-**5** and HPLC as well as by $^{19}$F NMR analysis of their Mosher esters (see Supplementary material,



Scheme 1.



Scheme 2.



Scheme 3.