Tetrahedron 66 (2010) 631–636

Contents lists available at ScienceDirect

Tetrahedron

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

Salen and half-salen palladium(II) complexes: synthesis, characteriztion and catalytic activity toward Suzuki–Miyaura reaction

Ping Liu, Xiu-Juan Feng, Ren He *

State Key Laboratory of Fine Chemicals, Dalian University of Technology (DUT), 158 Zhongshan Rd., 116012 Dalian, China

A R T I C L E I N F O

Article history:
Received 15 September 2009
Received in revised form
6 November 2009
Accepted 17 November 2009
Available online 4 December 2009

Keywords:
Salen and half-salen ligands
Palladium complexes
Suzuki–Miyaura reaction

A B S T R A C T

Salen and half-salen palladium(II) complexes (salden)Pd (**1**, salden=*N*,*N*′-bis(3,5-di- *tert*-butylsalicylidene)-1,2-dimethylethylenediamine), (hsalph)PdCl (**2**, hsalph=3,5-di-*tert*- butylsalicylidene-1-iminophenylene-2-amine), and (salph)Pd (**4**, salph=*N*,*N*′-bis(3,5-di-*tert*- butylsalicylidene)-1,2-phenylenediamine) were prepared and structurally characterized by X-ray crystallography. Complex **2** proved to exhibit high catalytic activity toward Suzuki–Miyaura reaction. Polyaromatic C_3-symmetric derivatives and various fluorinated biphenyl derivatives were readily achieved in good yields using Suzuki–Miyaura reaction catalyzed by complex **2**.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Palladium-catalyzed Suzuki–Miyaura reaction has been used extensively for the synthesis of natural products, pharmaceutical intermediates, conducting polymers, pesticides, and liquid crystals.[1,2] By far, phosphine-based ligands remains to be the most popular selection in this reaction.[3–9] However, most of the phosphine ligands are air- and moisture-sensitive, and P–C bond degradation sometimes occurs at elevated temperatures, which leads to palladium aggregation and eventually affects the overall catalytic performance.[10] Recent application of phosphine-free ligands, such as *N*-heterocyclic carbenes,[11–24] *N*,*N*,*O*-chelate ligand,[25] *N*,*O*- or *N*,*N*-bidentate ligands,[9,26–32] aryloximes,[33,34] arylimines,[35–39] *N*-acylamidines,[40] guanidine[41] and simple amines[42–47] to Pd-catalyzed Suzuki–Miyaura reaction has opened new opportunities. The design of novel palladium complexes bearing phosphine-free ligands, which show high catalytic activity and selectivity toward C–C bond forming reactions is becoming increasingly important. In our previous work, bis(imino)pyridine palladium(II) complexes have been used successfully to catalyze Suzuki–Miyaura reaction in water.[48,49] Herein, we describe the synthesis and characterization of air- and moisture-stable palladium(II) complexes bearing Salen or half-salen ligands and their catalytic activity toward Suzuki–Miyaura reaction.

2. Results and discussion

2.1. Synthesis of complexes 1–4

(Salden)Pd (**1**, salden=*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-dimethylethylenediamine) was prepared by the reaction of ligand $\mathbf{L_1}$ with $PdCl_2(CH_3CN)_2$ in ethanol for 12 h at room temperature. However, the reaction of ligand $\mathbf{L_2}$ with $PdCl_2(CH_3CN)_2$ in the same condition afford product **5**, rather than the expected complex (salph)Pd (**4**, salph=*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-phenylenediamine). We speculated that product **5** should consist of (hsalph)PdCl (**2**, hsalph=3,5-di-*tert*-butylsalicylidene-1-iminophenylene-2-amine) and **3**, which were formed by the reaction of $PdCl_2(CH_3CN)_2$ with ligand $\mathbf{L_3}$ and benzene-1,2-diamine derived from the hydrolyzation of ligand $\mathbf{L_2}$, respectively. To verify this hypothesis, complexes **2** and **3** were prepared by reaction of $PdCl_2(CH_3CN)_2$ with the corresponding ligands in EtOH. Comparative studies of ^1H NMR (Fig. 1), ^{13}C NMR, IR spectra, HRMS (EI), and element analysis indicated that product **5** surely consist of complexes **2** and **3** (molar ratio, **2**:**3**=4:1). Finally complex **4** was synthesized using another method that the $CHCl_3$ solution of ligand $\mathbf{L_2}$ reacted with the CH_3CN solution of $PdCl_2(CH_3CN)_2$ for 1 h at reflux condition (Scheme 1). The structures of complexes **1**, **2**, and **4** were further confirmed by X-ray crystallography. The crystal structures

---

* Corresponding author. Tel.: +86 0411 39893861; fax: +86 0411 39893687.
E-mail address: liuping1979112@yahoo.com.cn (R. He).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.11.072

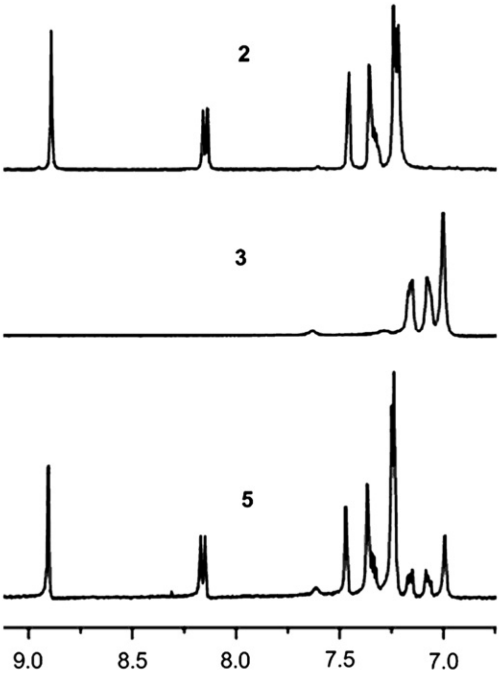


Figure 1. ^{1}H NMR spectra (aromatic region) of complexes **2**, **3**, and product **5** (400 MHz, DMSO-d_6).

of complexes **1**, **2**, and **4** are shown in Figures 2–4. Selected bond lengths and angles are summarized in Table 1. The geometries of **1**, **2** and **4** is a distorted square planar, and the Pd–N bond lengths (Pd(1)–N(1) 1.964(17) Å, Pd(1)–N(2) 2.025(19) Å) of **2** are slightly

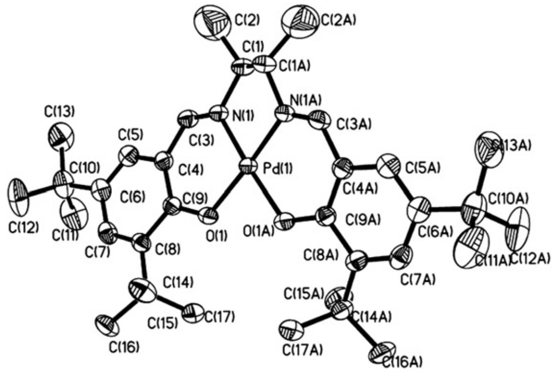


Figure 2. ORTEP drawing of complex **1**.

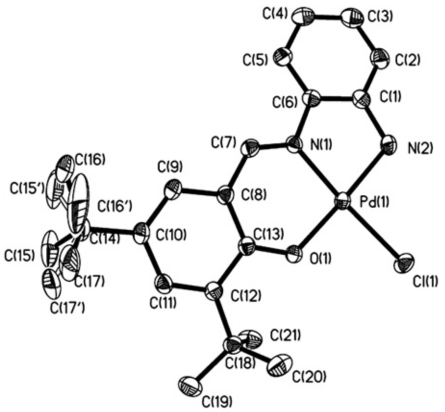
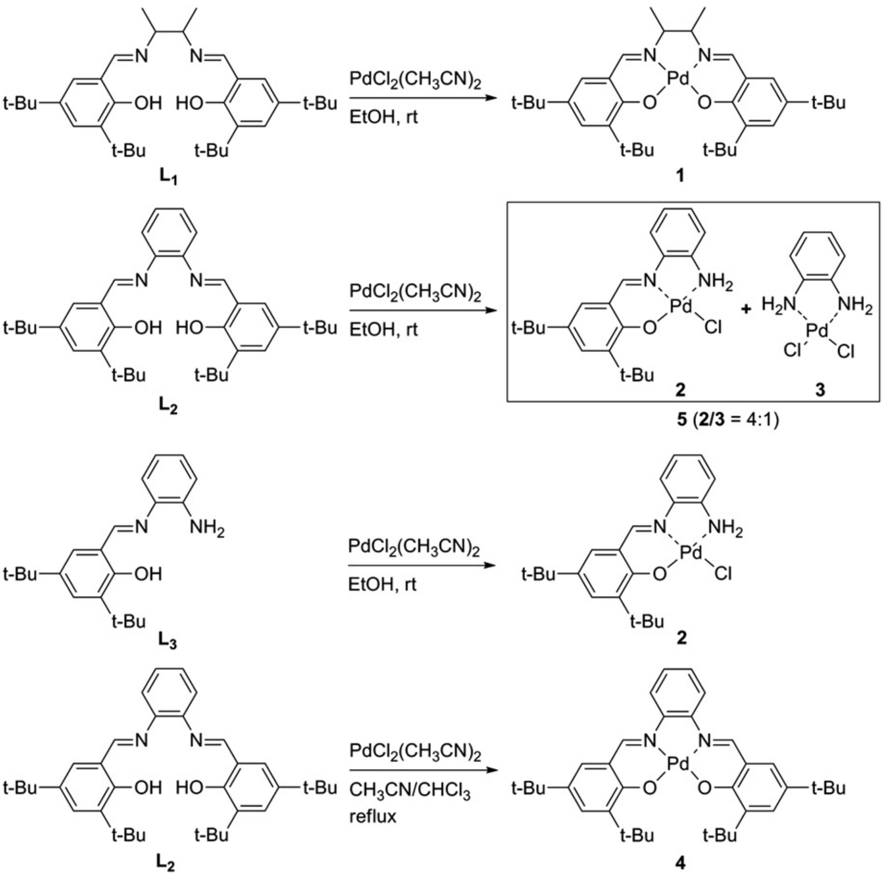


Figure 3. ORTEP drawing of complex **2**.



Scheme 1. Synthesis of complexes **1–4**.

Download English Version:

https://daneshyari.com/en/article/5225989

Download Persian Version:

https://daneshyari.com/article/5225989

Daneshyari.com