



# Synthesis of and ethylene oligomerization with binuclear palladium catalysts having sterically modulated bis-imine ligands with methylene spacer

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## ABSTRACT

Sterically modulated bis-imine ligands ( $L^1-L^3$ ) were prepared by reacting 4,4'-methylene bis-(2,6-dialkyl aniline) and antipyrine-4-carboxaldehyde in a 1:2 stoichiometric ratio. The reactions of  $L^1-L^3$  with dichloro(cycloocta-1,5-diene)palladium(II) [ $PdCl_2(cod)$ ] yield the corresponding binuclear palladium complexes with the general formula  $Pd_2Cl_4L$  ( $L = L^1, L^2, \text{ and } L^3$ ). The binucleating ligands bind to the palladium ion via the lone pair on the imine nitrogen and amide oxygen atoms, resulting in a square-planar geometry around the metal center. All the palladium catalysts efficiently oligomerize ethylene to produce  $C_4-C_{20}$  fractions at activities of up to  $1308 \text{ kg-oligomer mol-Pd}^{-1} \text{ bar}^{-1} \text{ h}^{-1}$  at  $30 \text{ }^\circ\text{C}$  in combination with ethylaluminum sesquichloride. The formation of active sites by the change in geometry of the metal complexes could be traced using spectroscopic and electrochemical techniques.

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## 1. Introduction

In the past decade, a new generation of oligomerization catalyst precursors has emerged with excellent activity, selectivity, living behavior, and stability [1–3]. In particular, ethylene oligomerization systems have been reported for nickel, iron, and chromium, but palladium-based catalysts constitute the most numerous, active, and selective group. Essentially, non-metallocene bis-imine based catalysts comprising of a bimetallic core separated by aliphatic or aromatic spacers were employed to achieve synergistic effects found in metallocene catalysts [4,5]. The ligand design of such systems is of fundamental importance, because the ligand structure defines the environment around the metal centers. Broadly speaking, there are two different types of bimetallic cores: a remote donor bimetallic core with aliphatic or aromatic spacers and an atom- or bond-bridged core. The former is of greater interest because the distance between the metals can be tuned using extended pi-bond conjugations through the spacers. Bimetallic palladium catalysts offer diverse and difficult challenges with regards to the design of new efficient catalyst systems for ethylene oligomerization. Linear  $\alpha$ -olefins have a wide range of applications [6]. The lower carbon numbers are overwhelmingly used as

comonomers in the production of polyethylene.  $C_4-C_8$  linear  $\alpha$ -olefins are used in the synthesis of linear aldehydes via hydroformylation reactions. They have also been employed in the production of poly- $\alpha$ -olefin synthetic lubricant base stock and surfactants. Higher linear  $\alpha$ -olefins are used in making surfactants for aqueous detergent formulations and hydrophobes in oil-soluble surfactants. At present, even-carbon-numbered  $\alpha$ -olefins are produced industrially, but mostly via non-selective oligomerization of ethylene [6].

The rapid expansion of this area, stimulated by the promising catalytic activity of palladium complexes, resulted in considerable contributions to polyethylene production. Antipyrine-4-carboxaldehyde is of particular interest due to the feasibility and flexibility of ligand design, which allows the introduction of sterically and electronically demanding features [7,8]. Phenyl and alkyl groups attached adjacent to functional chromophores such as amide carbonyls and aldehyde groups in the antipyrine ring make the derived ligand systems active for ethylene oligomerization. The required degree of hindrance can be obtained using the alkyl and phenyl groups, allowing chain termination after the formation of the desired oligomers. In order to achieve variable steric hindrance in the ligand systems, a series of bis-amines with different aliphatic groups can be used [9]. The most notable feature of the catalysts formed by these combinations is the presence of fixed methyl and phenyl substituents on one side of the metal and variable aliphatic substituents on the other side, which makes these ligands very

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suitable for ethylene oligomerization [4,10]. In this regard, a series of simple bis-imine ligands derived from 4,4'-methylene bis-(2,6-dialkyl aniline) and antipyrine-4-carboxaldehyde were studied for the preparation of palladium catalysts, resulting in bidentate ligation and a square-planar Pd coordination. As a continuation of our research into these catalysis, we herein report interesting results regarding ethylene oligomerization with a series of sterically modulated palladium catalysts.

## 2. Experimental

### 2.1. Materials for the preparation of catalysts

All reactions were performed under a purified nitrogen atmosphere using the standard Schlenk technique. Polymerization-grade ethylene (SK Co., Korea) was purified by passing through columns of Fisher RIDOX™ catalyst and molecular sieves 5A/13X. Organic solvents, namely, ethanol, methanol, and diethyl ether, were distilled over CaH<sub>2</sub> and stored over molecular sieves. Toluene was distilled over Na/benzophenone under nitrogen and stored over molecular sieves. The reagents antipyrine-4-carboxaldehyde, dichloro(cyclo-octa-1,5-diene)palladium(II) [PdCl<sub>2</sub>(cod)], 4,4'-methylene bis-(2,6-dimethyl aniline), 4,4'-methylene bis-(2,6-diethyl aniline), 4,4'-methylene bis-(2,6-diisopropyl aniline), and glacial acetic acid were purchased from Aldrich Chem. Co. and used without further purification. Unless noted otherwise, all reagents were purchased from commercial sources and used as received.

### 2.2. Physical methods

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> solvent on a Varian Gemini-2000 300 MHz spectrometer at room temperature using TMS as an internal reference. Analytical thin layer chromatography (TLC) was carried out using Merck 0.25 mm silica gel 60F pre-coated aluminum plates with fluorescent indicator UV254. All ligands were purified using a Combi-Flash (Companion) auto-column machine. Elemental analysis was carried out using a Vario EL analyzer. Infrared (IR) spectra were recorded as KBr discs (ligands) or CsI (catalysts) disc matrix using a Shimadzu IRPrestige-21 over a 4000–200 cm<sup>-1</sup> range. The electronic spectra of the complexes were recorded on a Shimadzu UV-1650PC spectrophotometer in the range of 1000–200 nm. Cyclic voltammetry (CV) studies were performed at room temperature in chloroform under O<sub>2</sub> free conditions using Kosentech Model CV-104. Mass spectra of catalysts were recorded using positive fast atom bombardment (FAB) methods on a JEOL JMS-700, HP 5890 Series II spectrometer. Thermogravimetric (TG) and differential thermal analysis (DTA) of the catalysts were performed under a nitrogen atmosphere on a DuPont 951 maintaining the final temperature at 800 °C and a heating rate of 10 °C/min under a nitrogen atmosphere. The oligomers were analyzed by gas chromatography (HP-6890) using a J&W Scientific DB608 column (30 mm 90.53 mm) equipped with a FID detector. The injector and detector temperature was kept constant at 250 °C. The initial temperature was set at 30 °C (hold 2 min) and finishing temperature at 250 °C (hold 10 min) with a heating rate of 10 °C/min.

### 2.3. Ethylene oligomerization

Ethylene oligomerization was performed in a 250 mL round-bottom flask equipped with a magnetic stirrer and a thermometer. High-dilution techniques were adopted to reduce the monomer mass transport effect. After addition of the catalyst, the reactor was charged with toluene (80 mL) via a syringe and immersed in a constant temperature bath previously set to a desired temperature.

When the reactor was equilibrated to the bath temperature, ethylene was pressurized into the reactor (1.3 bar) after removing the nitrogen gas under vacuum. When no more absorption of ethylene into toluene was observed, a prescribed amount of co-catalyst was injected into the reactor and oligomerization commenced. The oligomerization rate was determined every 0.01 s from the rate of consumption, measured by a hotwire flow meter (model 5850 D from Brooks Instrument Div.) connected to a PC through an A/D converter. Oligomerization was quenched by the addition of methanol containing HCl (5 v/v%) after cooling. The resulting mixture was passed through an alumina column to remove all aluminum containing species and the obtained oligomers were analyzed by gas chromatography. The rate of ethylene consumption was directly obtained from the computerized experimental apparatus and is expressed as in terms of g-product mol<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup>. In order to make a convincing assessment of the effects of catalyst structure on catalytic activity and oligomer distribution, all data were collected under similar conditions.

### 2.4. Detection of the active species

#### 2.4.1. <sup>1</sup>H NMR spectral technique

Alkyl-palladium active species were detected by *in-situ* <sup>1</sup>H NMR spectral technique under ethylene oligomerization conditions. Palladium catalyst (2.5 μmol) was introduced into an NMR tube under a nitrogen atmosphere and deuterated chloroform (0.7 mL) was added. The tube was saturated with ethylene gas, followed by the addition of ethylaluminum sesquichloride (EASC) (Al/Pd = 300). The <sup>1</sup>H NMR spectra of the reaction mixture was recorded as a function of time. The changes observed were correlated with a blank EASC spectrum as a control under similar conditions.

#### 2.4.2. Electronic spectral technique

For the detection of alkyl-palladium active species formed during oligomerization, UV–visible spectra of the catalysts were recorded under oligomerization conditions. Palladium catalyst (2.5 μmol) was added to a cuvette containing 1 mL of toluene in an inert atmosphere, and then saturated with ethylene gas (1.3 bar). EASC (Al/Pd = 300) was injected into the system to initiate oligomerization and the UV–visible spectra of the reaction mixture were recorded over time.

### 2.5. Syntheses

#### 2.5.1. Preparation of the ligands (L<sup>1</sup>–L<sup>3</sup>)

A methanolic solution of antipyrine-4-carboxaldehyde (0.432 g, 2 mmol) was added to a methanolic solution of 4,4'-methylene bis-(2,6-dimethyl aniline) (0.254 g, 1 mmol) in a 50 mL Schlenk flask under a nitrogen atmosphere. A catalytic amount of formic acid was added and the reaction mixture was kept at refluxing temperature for 4 h, and then cooled to room temperature. A pale yellow solid was separated by filtration and purified by column chromatography using hexane/ethyl acetate as eluant (8:2 v/v). The product (L<sup>1</sup>) was dried under vacuum at room temperature and stored in a vacuum desiccator. The reactions involved in the preparation of the ligands are outlined in Fig. 1. Yield: 46.3%. m.p.: 109–111 °C. Elemental analysis: Found (calculated) for C<sub>41</sub>H<sub>42</sub>N<sub>6</sub>O<sub>2</sub>: C 75.4 (75.7), H 6.9 (6.5), N 12.1 (12.9). FTIR (KBr disc) cm<sup>-1</sup>: 3384 ν (N–C, antipyrine ring), 2922 ν (C–H, alkyl), 1676 ν (>C=O, amide), 1599 ν (>C=N, imine), and 1076 ν (N–N, antipyrine ring). <sup>1</sup>H NMR (CDCl<sub>3</sub>) ppm: 8.4 (s, 2H, azomethine protons), 7.8–7.4 (m, 10H, aromatic protons), 6.9 (s, 4H, aromatic protons), 3.6 (s, 2H, methylene spacer protons), 3.1 (s, 6H, antipyrine N–Me protons), 2.4 (s, 6H, antipyrine C–Me protons), and 1.0 (s, 12H, methyl protons). <sup>13</sup>C NMR (CDCl<sub>3</sub>) ppm:

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