Journal of Organometallic Chemistry 696 (2011) 1465–1473

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Nickel and cationic palladium complexes bearing (imino)pyridyl alcohol ligands: Synthesis, characterization and vinyl polymerization of norbornene

Suyun Jie*, Pengfei Ai, Qimeng Zhou, Bo-Geng Li

State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, 38 Zheda Road, Hangzhou 310027, China

ARTICLE INFO

Article history:
Received 10 December 2010
Received in revised form
14 January 2011
Accepted 18 January 2011

Keywords:
Nickel
Palladium
Norbornene
Vinyl polymerization

ABSTRACT

A series of nickel and palladium complexes bearing (imino)pyridyl alcohol tridentate [N,N,O] ligands, 2-(ArN=CMe)-6-{(HO)CR_2}C_5H_3N (**L1**–**L4**), were synthesized and sufficiently characterized by elemental and spectroscopic analysis along with X-ray diffraction analysis. The X-ray diffraction demonstrated that five-coordinated nickel halide complexes (**1a**–**4a** and **1b**) and six-coordinated nickel acetate complex (**1c**) were prepared, and cationic palladium complexes (**1d** and **2d**) formed with the $[PdCl_4]^{2-}$ counterion. All these complexes displayed high catalytic activities up to 1.883×10^7 g(PNB) mol^{-1}(cat) h^{-1} (**2d**) for the vinyl polymerization of norbornene on treatment with excess methylaluminoxane (MAO), affording the vinyl-type PNBs with high molecular weights and relatively narrow molecular weight distributions. The parameters of reaction conditions, the type of metals and steric effects of coordinative ligands had influences on the catalytic properties.

1. Introduction

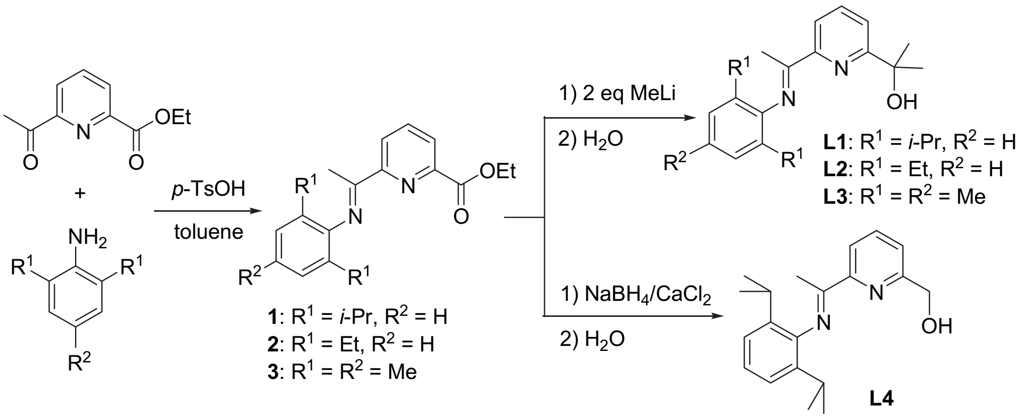
Norbornene (bicyclo[2.2.1]hept-2-ene, NB) and its derivatives can be polymerized in three different pathways: ring-opening metathesis polymerization (ROMP) [1], cationic or radical polymerization [2], and vinyl/addition polymerization [3]. Each route produces its own polymer type with different structures and properties and can be differentiated through various transition metal containing catalysts. Vinyl-type polymerization was first described in the early 1960s and cycloaliphatic polymers containing bicyclic structural units intact without any double bond were produced by using classical $TiCl_4$-based Ziegler catalyst [4]. With constrained rings in each unit, the vinyl-type norbornene polymers (PNBs) possess interesting and unique properties [5], such as high chemical resistance, good UV resistance, low dielectric constant, excellent transparency, low water uptake, large refractive index, small optical birefringence and dielectric loss, high glass transition and decomposition temperatures.

Catalysts containing the metals titanium, zirconium, chromium, and currently the late-transition metals cobalt, nickel and palladium are described in the literatures for the vinyl homo-polymerization of norbornene [3]. Nickel and palladium complexes especially have drawn much attention since the discovery of the α-diimine complexes of Ni and Pd for the polymerization of ethylene and α-olefins by Brookhart and coworkers [6]. Novak reported the first example of nickel complexes for the vinyl polymerization of norbornene in 1993 [7], and recently some of nickel and palladium complexes were also found to be highly active for the vinyl polymerization of norbornene, affording vinyl-type PNBs with molecular weights higher than 10^6 g/mol [3e]. Among the Ni and Pd precatalysts developed, most contained bidentate ligands, such as [N,O] [8], [N,N] [9], [P,N] [10], [P,P] [11]. However, only a few nickel and palladium complexes bearing tridentate [12] or multidentate [12a,13] ligands were reported for the vinyl polymerization of norbornene, of which tridentate phenoxy-imine ligands with an hydroxyl group or an alkoxyl group sidearms ([O,N,O]) [12a,b] and phenoxy-imine(quinoline) framework ([N,N,O]) [12f] were of interest for us. In order to develop new late-metal catalysts with tridentate ligands and confirm the function of phenoxy-O group, we synthesized the nickel and palladium complexes ligated by tridentate (imino)pyridyl alcohol tridentate [N,N,O] ligands, some of which had been used in an (1-adamantylimido)vanadium(V) complex [14] and iron(II) complexes showing moderate activities in ethylene polymerization [15]. In this paper, we will describe the synthesis and structures of nickel and cationic palladium complexes bearing a series of tridentate 2-arylimino-6-(alcohol)pyridine ligands and the evaluation of their catalytic properties for the vinyl polymerization of norbornene.

---

* Corresponding author. Tel.: +86 571 87952631; fax: +86 571 87951612.
E-mail address: jiesy@zju.edu.cn (S. Jie).

0022-328X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2011.01.024



Scheme 1. Synthesis of (imino)pyridyl alcohol ligands **L1**–**L4**.

2. Results and discussion

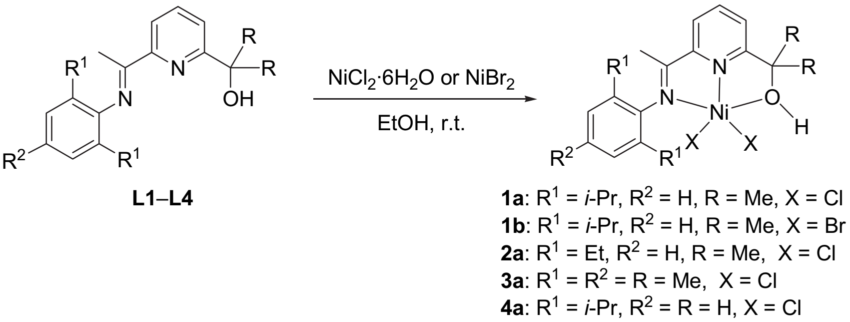
2.1. Synthesis of (imino)pyridyl alcohol ligands and their complexes

The starting materials, 2-carboxylate-6-iminopyridine compounds, 2-COOEt-6-(ArN=CMe)C_5H_3N (Ar = 2,6-i-$Pr_2C_6H_3$, **1**; 2,6-$Et_2C_6H_3$, **2**; 2,4,6-$Me_3C_6H_2$, **3**) [16], were readily accessible by the condensation reaction of 6-acetylpyridine-2-carboxylate and the corresponding substituted anilines. Those compounds had been developed by the group of Sun [16] and were proven to be effective as ligands for iron, cobalt, nickel, palladium and chromium complexes in catalytic ethylene polymerization/oligomerization [17]. The desired (imino)pyridyl alcohol ligands, 2-(ArN=CMe)-6-{(HO)CMe_2}C_5H_3N (Ar = 2,6-i-$Pr_2C_6H_3$, **L1**; 2,6-$Et_2C_6H_3$, **L2**; 2,4,6-$Me_3C_6H_2$, **L3**), were prepared by the slow addition of MeLi solution in THF into a solution of 2-carboxylate-6-iminopyridines (**1**–**3**) in THF at 0 °C, stirring at room temperature and subsequent hydrolysis (Scheme 1), which were obtained in high purity after separation by using column chromatography. The ligand **L4**, 2-(2,6-i-$Pr_2C_6H_3N$=CMe)-6-(CH_2OH)C_5H_3N, was prepared via the reduction of compound **1** by sodium borohydride with the assistance of calcium chloride in methanol in good yield (Scheme 1). All the ligands were identified on the basis of FT-IR, ^1H and ^{13}C NMR spectra as well as elemental analysis and some of them were compared with the reference data [14,15].

The nickel complexes **1a**–**4a**, **1b** and **1c** were readily prepared by mixing the corresponding ligand and one equivalent of $NiCl_2 \cdot 6H_2O$, $NiBr_2$ or $Ni(OAc)_2 \cdot 4H_2O$ in ethanol at room temperature and were isolated as orange or brown air-stable powders (Schemes 2 and 3). The reaction of ligands and $PdCl_2$ in ethanol at room temperature proceeded relatively slowly; therefore the preparation of palladium complexes **1d** and **2d** was requisite to be carried out at 60 °C for 3 h (Scheme 4). All the complexes were well characterized by FT-IR spectra and elemental analysis. In the IR spectra, the stretching vibration bands of C=N double bonds of these nickel and palladium complexes (1616–1620 cm^{-1}) apparently shifted to lower wave number and the peak intensity greatly reduced, as compared to the corresponding ligands (1642–1645 cm^{-1}), indicating the coordination interaction between the imino nitrogen atom and the metal center; and so did the hydroxyl group. The ^1H NMR spectra of palladium complexes **1d** and **2d** exhibited two sets of protons with slightly different chemical shifts. The molecular structures of complexes **1a**, **1c** and **2d** were further confirmed by the single-crystal X-ray diffraction analysis (Figs. 1–3).

2.2. Crystal structures

Single crystals of complex **1a** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into its methanol solution. The molecular structure is shown in Fig. 1, and the selected bond lengths and angles are listed in Table 1. According to its structure, the coordination geometry around the nickel center can be described as a distorted trigonal bipyramidal, in which the nitrogen of pyridyl group (N1) and two chlorides (Cl1 and Cl2) compose an equatorial plane and the nickel atom slightly deviates by 0.0774 Å from this triangular plane. The three equatorial angles N1–Ni–Cl1, Cl1–Ni–Cl2 and N1–Ni–Cl2 are respectively 95.42 (8)°, 109.46(5)° and 154.59(9)° with the larger distortion of N1–Ni–Cl2 and the axial Ni–N2 and Ni–O1 bonds subtend an angle of 150.10(10)° (O1–Ni–N2). The equatorial plane is nearly perpendicular to the pyridyl plane with a dihedral angle of 90.7°. The dihedral angle between the phenyl ring and the pyridyl plane is 126.4°. The Ni–N1 (pyridyl) bond (1.995(3) Å) in the equatorial



Scheme 2. Synthesis of nickel complexes **1a**–**4a** and **1b**.