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Syntheses of iron, cobalt, chromium, copper and zinc complexes with bulky bis(imino)pyridyl ligands and their catalytic behaviors in ethylene polymerization and vinyl polymerization of norbornene

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Abstract

The syntheses, characterization, and ethylene and norbornene polymerization behaviors of iron, cobalt, chromium, copper and zinc complexes (**3**–**7b**) bearing chelating bulky 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine ligand (**1**) or 2,6-bis[1-(2,5-ditertbutylphenylimino)ethyl]pyridine ligand (**2**) are reported. X-ray diffraction study of the cobalt complex (**4**) shows the geometry of the cobalt center to be distorted trigonal bipyramid. Treatment of the iron, cobalt 2,6-bis[1-(2,5-ditertbutylphenylimino)ethyl pyridine complexes (**3** and **4**) with methylaluminoxane (MAO) lead to a highly active ethylene polymerization catalysts converting ethylene to highly linear polyethylene (PE), while the corresponding chromium complex (**5**) is disclosed as moderate catalytic activity for the polymerization of ethylene. The specific catalytic activities were evaluated at different temperature and Al/M (M = Fe, Co and Cr) ratio. In addition, the complexes **3**–**5** and corresponding compounds of $FeCl_2$, $CoCl_2(THF)_{1.5}$ and $CrCl_3(THF)_3$ can also catalyze vinyl polymerization of norbornene activated with MAO and show good activities. However, the copper and zinc complexes (**6a**–**7b**) showed no active in ethylene and norbornene polymerization in the presence of MAO.

Keywords: Ethylene and norbornene polymerization; Bis(imino)pyridyl ligands; Iron; Cobalt; Chromium; Copper; Zinc

1. Introduction

Non-metallocene complexes have been shown to be important catalysts in the polymerization of olefins [1]. One of the most effective catalyst are Fe(II), Co(II) and Cr(II or III) *N*,*N*,*N*-bis(imino)pyridyl-type complexes [2]. Treatment of these complexes LMX_n (M = Fe, Co, Cr) with methylaluminoxane (MAO) leads to highly active ethylene polymerization catalysts converting ethylene to highly linear polyethylene (PE) or oligomerization. Several modifications of the bis(imino)pyridine backbone, which have already been described in the literature [1b,3–5], mostly lead to a decrease in catalytic activity. Recently, simultaneous polymerization and Schulz–Flory oligomerization of ethylene made possible by activation with MAO of a C_1-symmetric [2,6-bis(arylimino)pyridyl]iron dichloride precursor were described [6], as were bis(imino)pyridine complexes containing dendritic wedges [7] and metallodendrimer [8].

The NBE (norbornene) addition polymer displays a characteristic rigid random coil conformation, which shows restricted rotation about the main chain and exhibits strong thermal stability ($T_g > 350\,°C$). In addition, it has excellent dielectric properties, optical transparency and unusual transport properties. Therefore, it has been attracted many chemists to study the NBE vinyl polymerization. In recent years, the vinyl-type polynorbornene (PNB) can be prepared by nickel-based complexes and other metal complexes [9–15]. Yasuda et al. [16] reported several cobalt complexes bearing substituted terpyridine ligands for vinyl norbornene polymerization. Frédéric et al. [17] reported polymerization of NBE with $CoCl_2$ and pyridine bisimine cobalt(II) complexes activated with MAO. Janiak and co-workers [18] reported dihalogeno(diphosphane)metal(II) complexes (metal = Co, Ni, Pd) as pre-catalysts for the vinyl/addition polymerization of norbornene-elucidation of

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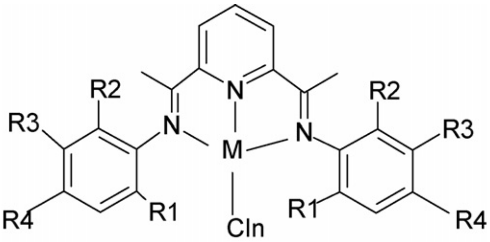

Fig. 1. Iron, cobalt and chromium bis(imino)pyridyl precatalysts for the polymerization of ethylene.

the activation process with $B(C_6F_5)_3/AlEt_3$ or Ag[closo-1-$CB_{11}H_{12}$]. Janiak and co-workers [19] also reported novel polynuclear cage complexes as precatalysts in the vinyl or addition polymerization of norbornene activated with MAO as well as with $B(C_6F_5)_3$, in combination with or without $AlEt_3$ and correlated with the results of the known mononuclear precatalysts $M(acac)_x$ ($M = Ni^{II}$, Co^{III}, Cr^{III} and Fe^{III}, acac = acetylacetonate, $x = 2$ or 3).

The nature of the metal center has a large influence on catalyst productivity. In general, Fe catalysts are more active than the corresponding Co analogues. It is well known that the position and steric bulk of the substituents on the imino nitrogen donors of the bis(imino)pyridyl catalysts (Fig. 1) play a pivotal role in determining the selectivity of the catalyst. The *ortho* substituents (R_1 and R_2) have been identified as being particularly important. If only one of the *ortho* substituents R_1 or R_2 on each ring is an alkyl group and the other is a hydrogen or halogen [4], then the catalyst is selective for the oligomerization of ethylene to linear 1-alkenes with a Schultz–Flory chain length distribution. If both the *ortho* substituents R_1 and R_2 groups are bulky alkyl substituents such as *iso*-propyl groups, then the catalysts are selective for the production of high molecular weight polymers from ethene.

To date, reports on olefin polymerization catalysts based on copper are scarce [1b]. The α-diimine Cu^{II} complex produces very high-molecular-weight PE with moderate activity [20]. Although there have been no reports of single-site olefin polymerization catalysts based on Group 12 metals, it has recently been shown that transition metal catalysts can catalyze PE chain growth on zinc centers, affording linear alkanes or α-olefins with a Poisson distribution [21]. The effect of substituents in the *meta*-position has been less studied [4,5d]. Here we report the syntheses, structures and ethylene and norbornene additional polymerization behaviors of iron, cobalt, chromium, copper and zinc complexes bearing bulky bis(imino)pyridyl ligands with 2,6-diisopropylphenyl or 2,5-ditertbutylphenyl substituents. We also report the effects observed on variation of the reaction conditions, such as the concentration of methylaluminoxane (MAO) and the temperature of ethylene polymerization. The results show that iron and cobalt bis(imino)pyridine complexes are highly active in the polymerization of ethylene by activation with MAO, while the corresponding chromium complex is disclosed as moderate active for the polymerization of ethylene. The iron and cobalt and chromium complexes show good active for the vinyl norbornene polymerization. However, the copper and zinc complexes almost show no active neither for the polymerization of ethylene nor vinyl norbornene polymerization in the presence of MAO.

2. Experimental

All manipulations of air and/or moisture-sensitive compounds were performed under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried prior to use by refluxing over and distillation from sodium (THF, toluene, hydrocarbons) or calcium hydride (dichloromethane, chlorobenzene). Norbornene (Across) was purified by distillation over sodium and used as a solution in chlorobenzene. IR spectra were recorded using a Nicolet AV-360 spectrometer. Elemental analyses were Perkin-Elmer 2400 elemental analyzer for C, H, N. 2,6-Diacetylpyridine, 2,5-ditertbutylaniline were purchased from Aldrich; MAO (10% solution in toluene) was obtained from Witco. $CoCl_2(THF)_{1.5}$ and $CrCl_3(THF)_3$ was prepared according to a published procedure [22]. Anhydrous $CuCl_2$ and $ZnCl_2$ were obtained from the corresponding aqueous salts which heated up under vacuum condition.

2.1. Synthesis of 2,6-bis[1-(2,6-diisopropylphenylimino) ethyl]pyridine (1)

2,6-Bis[1-(2,6-diisopropylphenylimino)ethylpyridine was synthesized according to the public literature [2c]. IR (KBr): 3063.2, 2960.6, 2926.7, 2867.4, 1643.2 (vs, C=N), 1577.56, 1457.55, 1383.5, 1364.6, 1322.5, 1240.1, 1192.4, 1118.3, 1077.6, 935.9, 875.7, 825.6, 767.5 and 689.2. Anal. Calcd for $C_{33}H_{43}N_3$: C, 82.20; H, 8.93; N, 8.72. Found: C, 82.45; H, 9.01; N, 8.45.

2.2. Synthesis of 2,6-bis[1-(2,5-ditertbutylphenylimino) ethyl]pyridine (2)

To a solution of 2,6-diacetylpyridine (0.50 g, 3.07 mmol) in absolute ethanol (20 ml) was added 2,5-ditertbutylphenyaniline (1.258 g, 6.14 mmol). After the addition of a few drops of glacial acetic acid, the solution was refluxed overnight. Upon cooling to room temperature, the product crystallized from ethanol. The yellow solid formed was then filtered and washed with cold ethanol and dried under vacuum; the yield was 86%. IR (KBr): 2958.8, 2866.8, 1635.6 ($\nu_{C=N}$), 1566, 1491, 1457.7, 1385.5, 1363.6, 1297.6, 1248.9, 1205, 1119.5, 1072, 974, 927, 886, 820, 722 and 652 cm^{-1}. Anal. Calcd for $C_{37}H_{51}N_3$: C, 82.68; H, 9.49; N, 7.82. Found: C, 82.75; H, 9.52; N, 7.71.

2.3. Synthesis of 2,6-bis[1-(2,5-ditertbutylphenylimino) ethyl]pyridineiron(II) chloride (3)

Ligand **2** (107 mg, 0.2 mmol) was added to a suspension of $FeCl_2$ (25 mg, 0.2 mmol) in CH_2Cl_2 (15 ml) at room temperature with rapid stirring. The solution turned deep blue immediately. After it was stirred at room temperature for 12 h, the excess $FeCl_2$ was removed. The reaction volume was concentrated, and *n*-hexane (30 ml) was added to precipitate the product as a blue powder, which was subsequently washed