Cobalt and Nickel Complexes Bearing 2-(2-pyridyl)-Benzimidazole: Synthesis and Ethylene Oligomerization

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Abstract: A series of cobalt and nickel complexes MLX_2 ($M = Co$ or Ni , $X = Cl$) bearing 2-(2-pyridyl)benzimidazole ligands were synthesized. Treatment of the complexes with methylaluminoxane (MAO) leads to active catalysts for ethylene oligomerization. The oligomers were olefins from C_4 to C_6 .

Key words: Nickel; Cobalt; Benzimidazole; Ethylene oligomerization

Introduction

Olefin polymerization and oligomerization promoted by transition metal complexes have drawn much attention in both academic research and industrial applications.¹⁻² Recent progress was reported by Brookhart and co-workers who showed that $Ni(II)$ and $Pd(II)$ complexes bearing bulky α -diimine ligands convert both ethylene and α -olefins to high molecular mass polymers with varying and controllable degrees of branching.³⁻⁴ Moreover, in parallel studies, Brookhart, Bennett and Gibson groups reported highly active polymerization catalysts based on $Fe(II)$ and $Co(II)$ incorporating 2,6-bis(imino)pyridyl ligands.⁵⁻⁶ Grubbs group reported new neutral $Ni(II)$ salicylaldiminato complexes as catalyst for the polymerization of ethylene under moderate conditions.⁷ Modification the substituents of aryl and imine carbon ligand result in dramatic changes to the activity of the catalyst and physical properties of the polyolefin.⁸⁻¹⁰ We were interested in exploring the effect of changing the central moiety to other nitrogen-containing heterocycles.¹¹ Here we describe the synthesis of $Co(II)$ and $Ni(II)$ complexes bearing 2-(2-pyridyl) benzimidazole ligands, as well as their oligomerization of ethylene study with MAO as co-catalyst.

Scheme 1. Synthesis of ligands and complexes

Result and Discussion

Synthesis and characterization

The 2-(2-pyridyl)benzimidazole ligands **1a~1c** were prepared as white or pale yellow solids in good yields by the condensation of one equivalent of the appropriate *o*-phenylenediamine with one equivalent of picolinic acid (Scheme 1). Compounds **1a~1c** were characterized by microanalysis and ^1H NMR. Complexes of these ligands were synthesized by dissolving nickel or cobalt chloride in ethanol (Scheme 1), followed by addition of one equivalent of the ligand in ethanol. The complexes precipitated from the reaction solution. After washing with diethyl ether, the complexes **2a~c** and **3a~c** were obtained in good yield and high purity. The elemental analysis results revealed that the components of all complexes were in accord with the formula MLX_2 .

Oligomerization of ethylene

Upon treatment with methylaluminoxane (MAO), all of the complexes are active ethylene oligomerization catalysts. Table 1 lists their activity and molecular weight distribution of the oligomers. The nature of the metal center has a major influence on catalytic activities. In general, Ni(II) catalysts are more active than their corresponding Co(II) analogues under same condition. The most active Ni(II) catalyst is complex **3a** ($1.14 \times 10^5 \text{ g(ethylene)mol}^{-1}(\text{Ni})\text{h}^{-1}$). While the Co(II) complexes are about $10^3 \text{ g(ethylene)mol}^{-1}(\text{Co})\text{h}^{-1}$ for oligomerization. Steric and electronic environmental around the central metal affected the catalytic activities. In the same condition, catalysts (**2c**, **2b**, **2a**; **3c**, **3b**, **3a**) reveal that electron-donating group replacing the proton results in decreases in activity. The complex **2a** (**3a**) contains two methyl groups in the aryl rings and displays an activity of 5.78×10^3 (0.52×10^5) $\text{g(ethylene)mol}^{-1}(\text{M})\text{h}^{-1}$, approximately complex **2b** (**3b**) with one methyl in the aryl ring with an activity of 6.25×10^3 (1.04×10^5) $\text{g(ethylene)mol}^{-1}(\text{M})\text{h}^{-1}$. The same phenomenon was observed in our previously research.¹¹⁻¹² The oligomers are from C_4 to C_6 . The substituents of the complexes affect distribution of the oligomers to some extent.

Experimental

MAO (1.4 mol l^{-1}) was purchased from Albemarle Corp (USA); Nickel or cobalt chloride and all of the *o*-phenylenediamines were used commercially without further purification. C, H, N elemental analysis was performed using CHN-RAPID microanalyzer. ^1H NMR spectra were recorded on a Bruker spectrometer DMX-300, with TMS as the internal standard. Melting points were determined without

further correction. Ethylene oligomerization results were recorded on a HP5890 Series II gas chromatograph (Hewlett-Packard).

General procedure of synthesis ligands

A mixture of *p*-phenylenediamine (5 mmol), picolinic acid (5 mmol) and PPA (4.5 g) was stirred at 160 °C for 5 h under N₂. After cooled to 100 °C, it was poured into 30 mL water. The solution was cooled and added Na₂CO₃ to adjust pH to 7. The precipitated solid was filtered and recrystallized from AcOEt.

(**1a**): yield 61%, m.p. 229-230 °C, ¹H-NMR(CDCl₃): δ 10.63 (1H, br), 7.33-8.69 (8H, m). Anal. Calc. for C₁₂H₉N₃: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.85; H, 4.65; N, 21.46%.

(**1b**): yield 66%, m.p. 165-166 °C, ¹H-NMR(CDCl₃): δ 10.35 (1H, br), 7.13-7.89 (7H, m), 2.52 (3H, s). Anal. Calc. for C₁₃H₁₁N₃: C, 74.62; H, 5.30; N, 20.08. Found: C, 74.80; H, 5.17; N, 20.05%.

(**1c**): yield 71%, m.p. 194-195 °C, ¹H-NMR(CDCl₃): δ 10.15 (1H, br), 7.26-8.62 (6H, m), 2.39 (6H, s). Anal. Calc. for C₁₄H₁₃N₃: C, 75.31; H, 5.87; N, 18.82. Found: C, 78.90; H, 7.89; N, 13.15%.

General procedure of synthesis complexes

MCl₂ · 6H₂O (0.20 mmol) in 5 mL ethanol and ligand (0.20 mmol) in 5 mL ethanol were combined in a Schlenk flask. The mixture was stirred at room temperature for 10 hours, then the crude product was collected by filtration, washed with 3×4 mL of Et₂O.

(**2a**): yield 93%. Anal. Calc. for C₁₂H₉N₃CoCl₂: C, 44.34; H, 2.79; N, 12.93. Found: C, 44.44; H, 2.75; N, 12.96%.

(**2b**): yield 85%. Anal. Calc. for C₁₃H₁₁N₃CoCl₂: C, 46.05; H, 3.27; N, 12.39. Found: C, 46.05; H, 3.39; N, 12.18%.

(**2c**): yield 90%. Anal. Calc. for C₁₄H₁₃N₃CoCl₂: C, 47.62; H, 3.71; N, 11.90. Found: C, 46.40; H, 3.76; N, 11.63%.

(**3a**): yield 85%. Anal. Calc. for C₁₂H₉N₃NiCl₂: C, 44.37; H, 2.79; N, 12.94. Found: C, 44.16; H, 2.85; N, 12.62%.

(**3b**): yield 87%. Anal. Calc. for C₁₃H₁₁N₃NiCl₂: C, 46.08; H, 3.27; N, 12.40. Found: C, 46.53; H, 3.21; N, 12.25%.

(**3c**): yield 90%. Anal. Calc. for C₁₄H₁₃N₃NiCl₂: C, 47.45; H, 3.71; N, 11.91. Found: C, 47.20; H, 3.40; N, 11.67%.

General Procedure for Ethylene Oligomerization

A flame dried three-neck round flask was evacuated-filled three times by nitrogen. Then ethylene was charged with 30 mL of freshly distilled toluene and stirred. At the room temperature, the aluminum cocatalyst MAO was added via syringe. The solution was stirred and the precatalyst complex (**2a-c** or **3a-c**, 10⁻³ mol in 5 mL toluene) was added to the reaction mixture via syringe. After stirred under 1 atm ethylene pressure for 20 min, the oligomerization was terminated by acidified ethanol. An aliquot of the reaction mixture was analyzed by gas chromatography. Their activity and distribution of the oligomers were collected in **Table 1**.

Table 1. Activity and distribution for the oligomerization

Complex	Al/Ni	Activity (g/mol h atm)	Distribution of oligomers (%)	
			C ₄	C ₆
2a	500	7.50×10 ³	62.03	37.97
2b	500	6.25×10 ³	69.09	30.91
2c	500	5.78×10 ³	72.74	27.26
3a	500	1.14×10 ⁵	80.44	19.56
3b	500	1.04×10 ⁵	78.51	21.49
3c	500	0.52×10 ⁵	72.65	27.35

Condition: [Al]/[Ni]=1500, toluene solvent, 1 atm of ethylene.

Conclusions

In summary, we have synthesized a series of nickel and cobalt complexes, upon treatment with MAO, they are all active ethylene oligomerization catalysts. Comparing with cobalt complexes showing marginal activity, nickel complexes show good activity. The oligomers are C₄ and C₆.

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