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Cobalt and Nickel Complexes Bearing 2,6-Bis(imino)phenoxy Ligands: Synthesis and Ethylene Oligomerization Study

JIAN-LONG DU* and LI-JUN LI

College of Chemistry and Environmental Science
Hebei University, Baoding 071002, P.R. China

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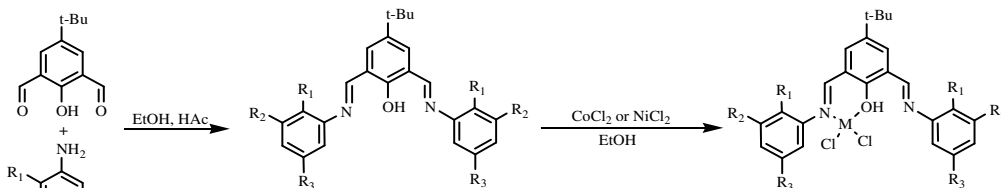
Abstract: A series of new cobalt and nickel complexes MLX_2 ($M = Co$ or Ni , $X = Cl$) bearing 2,6-bis(imino)phenoxy ligands have been synthesized. Treatment of the complexes with methylaluminoxane (MAO) leads to active catalysts for ethylene oligomerization. The oligomers are olefins from C_4 to C_6 .

Keywords: Nickel, cobalt, 2,6-bis(imino)phenoxy, ethylene oligomerization

Introduction

Late-transition metal complex as catalyst for olefin polymerization and oligomerization is an intense subject of academic research and industrial application.¹⁻² Recent progress was employing cationic Ni(II) bis(imino) complexes as effective catalysts for ethylene oligomerization and polymerization.³⁻⁵ Brookhart, Bennett and Gibson had made great contribution to design highly active ethylene polymerization catalysts based on iron (II) and cobalt (II) bearing 2,6-bis(imino)pyridyl ligands.⁶⁻⁸ Moreover, Grubbs reported new neutral Ni (II) salicylaldiminato complexes as catalysts for the polymerization of ethylene to obtain high molecular weight polyolefin under moderate conditions.⁹ Modification of the

substituents of imino groups results in dramatic changes to the resultant polyolefin.¹⁰ Sun also reported a series of salicylaldiminato complexes as catalysts for the polymerization of ethylene.¹¹ Now we focus on exploring the effect of changing the central pyridyl moiety to phenol. Herein, we report the synthesis of Co(II) and Ni(II) complexes bearing 2,6-bis(imino)phenoxy ligands and their ethylene oligomerization activity.



Scheme 1. Synthetic procedure for the catalysts

Experimental

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and Cannula techniques. Using HP-MOD 1106 microanalyzer performed elemental analysis. NMR spectra were recorded on a Bruker spectrometer DMX-300, with TMS as the internal standard. IR spectra were obtained as KBr pellets on a Perkin-Elmer FTIR 2000 spectrometer. Mass Spectra were measured on a Kratos AEI MS-50 instrument using electron impact (EI). Melting points were determined without further correction. Ethylene oligomerization results were recorded on a HP5890 Series II gas chromatograph (Hewlett-Packard).

Compound 2-hydroxy-5-tert-butylisophthaldehyde was prepared according to an established procedure.¹⁴ While MAO (1.4 mol l⁻¹) was purchased from Albemarle Corp (USA); Nickel or cobalt chloride and all of the anilines were used commercially without further purification unless stated otherwise.

Preparation of ligands

(L₁): To a solution of 2-hydroxy-5-tert-butylisophthaldehyde (0.62 g, 3 mmol) with a few drops of glacial acetic acid in anhydrous ethanol 15 mL under N₂ at 50 °C was added a solution of 2,3-dimethylaniline (0.73 g, 6 mmol) in anhydrous ethanol (10 ml) over a period of 20 min with stirring. Then the mixture was refluxed for additional 2h. Upon cooling to room temperature, the volatiles were removed under vacuum, and the residue was recrystallized from ethanol giving the yellow crystals 0.87 g in 70% yield, mp. 131-133°C. ¹H-NMR(CDCl₃), δ, ppm: 13.96 (1H, s), 8.79 (2H, br), 6.94-7.16 (6H, m), 2.34-2.36 (12H, m), 1.57 (6H, s), 1.42 (9H, s). IR(KBr), cm⁻¹: 3593 (m), 2963 (s), 1622, 1574 (vs), 1465 (s), 1377, 1309, 1284, 1239, 1219, 1091, 1035, 1009 (s), 888, 782 (s). EI-MS (m/z): 412 (M⁺, 3.5%), 293 (M⁺-NAr^r, 7.4%), 292 (M⁺-NAr^r-H, 43.7%), 291 (M⁺-NAr^r-2H, 100%), 277 (4.4%), 132 (8.7%), 120 (5.4%), 105 (8.7%). Anal. Calcd For C₂₈H₃₂N₂O: C, 81.51; H, 7.82; N, 6.79. Found: C, 81.44; H, 7.81; N, 6.82%.

(L₂): By using the procedure described above for synthesis of L₁, the ligand L₂ was obtained by the reaction of 2-hydroxy-5-tert-butylisophthaldehyde with 2, 5-dimethylaniline as a red crystals 1.06 g in 85% yield, mp. 151-153°C. ¹H-NMR(CDCl₃), δ, ppm: 14.06 (1H, s), 8.79 (2H, br), 6.90-7.15 (6H, m), 2.38 (12H, s), 1.57 (6H, s), 1.42 (9H, s). IR(KBr), cm⁻¹: 3436 (m), 2963 (s), 1617, 1570 (vs), 1465 (s), 1373, 1290, 1218, 1155, 1009 (s), 877, 765(s).

EI-MS (m/z): 412 (M^+ , 6.2%), 292 (M^+ -NAr'-H, 42.6%), 291 (M^+ -NAr'-2H, 100%), 277 (4.3%), 132 (6.5%), 120 (6.3%), 105 (7.7%). Anal. Calcd For $C_{28}H_{32}N_2O$: C, 81.51; H, 7.82; N, 6.79. Found: C, 81.55; H, 7.84; N, 6.78%.

(**L₃**): By using the procedure described above for synthesis of **L₁**, the ligand **L₃** was obtained by the reaction of 2-hydroxy-5-tert-butylisophthaldehyde with 3, 5-dimethylaniline as a red powder 0.93 g in 75% yield. mp. 61-62°C. 1H -NMR($CDCl_3$), δ , ppm: 14.04 (1H, s), 8.86 (2H, br), 6.94 (6H, s), 2.38 (12H, s), 1.57 (6H, s), 1.41 (9H, s). IR(KBr), cm^{-1} : 3486 (m), 2959 (s), 1622, 1579 (vs), 1465 (s), 1359, 1264, 1222, 1150, 1006 (s), 849, 765 (s). EI-MS (m/z): 412 (M^+ , 100%), 411 (M^+ -H, 12.8%), 292 (M^+ -NAr'-H, 52.2%), 291 (M^+ -NAr'-2H, 18.0%), 277 (5.2%), 132 (9.6%), 120 (3.6%), 105 (22.6%). Anal. Calcd For $C_{28}H_{32}N_2O$: C, 81.51; H, 7.82; N, 6.79. Found: C, 81.52; H, 7.83; N, 6.76%.

Preparation of complexes

Complex (1): $CoCl_2 \cdot 6H_2O$ (1mmol) and **L₁** (1mmol) were combined in a Schlenk flask under an N_2 atmosphere. EtOH (10 mL) was added, and the mixture was stirred at room temperature for 10 hours. The crude product was filtrated, washing with diethyl ether and the product was recrystallized from ethanol afford complex 1 as a green powder 0.46 g in 85% yield. IR(KBr), cm^{-1} : 3417 (m), 2961 (m), 1636 (vs), 1596 (s), 1537 (s), 1467 (m), 1363, 1325, 1292, 1232, 1071 (s). Anal. Calcd For $C_{28}H_{32}N_2O \cdot CoCl_2 \cdot H_2O$: C, 60.12; H, 5.95; N, 5.01. Found: C, 59.89; H, 6.11; N, 4.97%.

Complex (2): Using the procedure described above, the reaction of **L₂** and $CoCl_2 \cdot 6H_2O$ gave complex 2 0.42 g in 78% yield as a green powder. IR(KBr), cm^{-1} : 3438 (m), 2961 (m), 1641 (s), 1616 (s), 1538 (s), 1461 (m), 1362, 1325, 1282(w), 1238, 1060 (s). Anal. Calcd For $C_{28}H_{32}N_2O \cdot CoCl_2$: C, 62.00; H, 5.95; N, 5.16. Found: C, 61.89; H, 5.92; N, 5.17%.

Complex (3): Using the procedure described above, the reaction of **L₂** and $CoCl_2 \cdot 6H_2O$ gave complex 3 0.44 g in 81% yield as a green powder. IR(KBr), cm^{-1} : 3435 (m), 2960 (m), 1638 (s), 1591(s), 1539 (m), 1479 (m), 1239, 1201, 1145 (m), 1078, 1028 (s). Anal. Calcd For $C_{28}H_{32}N_2O \cdot CoCl_2$: C, 62.00; H, 5.95; N, 5.16. Found: C, 61.87; H, 5.87; N, 5.19%.

Complex (4): Using the procedure described above, the reaction of **L₁** and $NiCl_2 \cdot 6H_2O$ gave complex 4 0.41 g in 75% yield as a brown powder. IR(KBr), cm^{-1} : 3382 (m), 2961 (m), 1647 (s), 1577 (s), 1537 (m), 1466 (m), 1404, 1357, 1327, 1289, 1233, 1164 (m), 1046 (s). Anal. Calcd For $C_{28}H_{32}N_2O \cdot NiCl_2$: C, 62.03; H, 5.95; N, 5.17. Found: C, 62.08; H, 5.93; N, 5.29%.

Complex (5): Using the procedure described above, the reaction of **L₂** and $NiCl_2 \cdot 6H_2O$ gave complex 5 0.42 g in 78% yield as a brown powder. IR(KBr), cm^{-1} : 3370 (m), 2959 (m), 1649 (s), 1539 (s), 1454 (s), 1410, 1354, 1326, 1292 (w), 1238, 1118 (s). Anal. Calcd For $C_{28}H_{32}N_2O \cdot NiCl_2 \cdot H_2O$: C, 60.03; H, 6.12; N, 5.00. Found: C, 60.13; H, 6.10; N, 4.97%.

Complex (6): Using the procedure described above, the reaction of **L₃** and $NiCl_2 \cdot 6H_2O$ gave complex 6 0.42 g in 78% yield as a brown powder. IR(KBr), cm^{-1} : 3380 (br), 2960 (m), 1638 (s), 1536 (s), 1364, 1330, 1292(w), 1239, 1200 (m), 1143 (w), 1064, 1024 (s), 853 (s). Anal. Calcd For $C_{28}H_{32}N_2ONiCl_2$: C, 62.03; H, 5.95; N, 5.17. Found: C, 62.13; H, 5.70; N, 5.31%.

General procedure for ethylene oligomerization

A flame dried three-neck round flask was vacuated-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 (1 - 6, 5 μmol in 5ml 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 using gas chromatography. Their activity and distribution of the oligomers were collected in Table 1.

Table 1. Activity and Distribution of the Oligomerization^a

Complex	Al/Ni	Activity (g/mol·h·atm)	Distribution of oligomers (%)	
			C ₄	C ₆
1	500	3.65×10 ³	72.22	27.28
2	500	2.38×10 ³	74.71	25.29
3	500	1.78×10 ³	73.80	26.20
4	500	4.57×10 ⁴	69.27	30.73
5	500	2.82×10 ⁴	67.33	32.67
6	500	1.98×10 ⁴	65.97	34.03

^a Condition: Toluene solvent, 1atm of ethylene, T=15°C.

Results and Discussion*Synthesis and characterization*

2,6-bis(imino)phenoxy ligands L₁ - L₃ were prepared in good yields by condensation of one equivalent of the appropriate aniline with one equivalent of 2-hydroxy-5-tert-butylisophthaldehyde (Scheme 1). Compounds L₁ - L₃ were characterized by microanalysis, ¹H-NMR and mass spectrometry. The complexes 1 - 6 were synthesized by dissolving nickel chloride or cobalt chloride in ethanol (Scheme 1), followed by addition of one equivalent of ligand. The complexes precipitated from the reaction solution. After recrystallized from ethanol, the complexes were obtained in good yields and high purity. All the complexes were confirmed with elemental analysis and IR spectroscopy. The elemental analysis results revealed that the components of all complexes were in accord with the formula MLX₂.

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 the same condition. The most active Ni(II) catalyst is complex 1 (4.57×10⁴ g(ethylene)mol⁻¹(Ni)h⁻¹), While the Co(II) complexes are about 10³ g(ethylene)mol⁻¹(Co)h⁻¹ for oligomerization. Complexes 1 - 3 (4 - 6) revealed that a reduction of steric methyl at the *ortho*-aryl position resulted in the decrease of their activities, and electronic environmental around the central metal affected the catalytic activities. In the same condition, catalysts 1 (4) are more active than the catalysts 3 (6). Without methyl group in the aryl rings and 3 (6) displays an activity of 1.78×10³ (1.98×10⁴) g(ethylene)mol⁻¹(M)h⁻¹, approximately complex 1 (4) with one methyl at the *ortho*-aryl with an activity of 3.65×10³ (4.57×10⁴) g(ethylene)mol⁻¹(M)h⁻¹. The same phenomenon was observed in previously research.¹²⁻¹³ The oligomers are from C₄ to C₆. The substituents of the complexes affect distribution of the

oligomers to some extent. Comparing with the 2,6-bis(imino)pyridyl ligands⁶⁻⁸, when we change the central pyridyl moiety to phenol, their complexes only show oligomerization activity, no polymerization activity; at the same time, the selectivity in ethylene conversion are not very well.

Conclusions

We have synthesized six cobalt and nickel complexes. Upon treatment with methylaluminoxane, they are all active ethylene oligomerization catalysts. The oligomers are from C₄ to C₆.

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