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Ni(II) complexes bearing 2-aryliminobenzimidazole: synthesis, structure and ethylene oligomerization study

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Abstract

A series of nickel complexes bearing 2-aryliminobenzimidazole ligands were synthesized. Single-crystal X-ray analysis of complex **2** shows the nickel center adopts a distorted square-pyramidal geometry. Treatment of the complexes with methylaluminoxane (MAO) leads to active catalysts for ethylene oligomerization.

Keywords: Nickel complex; Schiff base; Ethylene oligomerization; Crystal structure

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In recent years there has been increasing interest in the development of late transition metal based complexes as catalysts for the polymerization and oligomerization of olefins [1,2]. The significant achievement by Brookhart group 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, Brookhart and Gibson groups individually reported highly active polymerization catalysts based on Fe(II) and Co(II) incorporating 2,6-bis(imino)pyridyl ligands [5,6]. Modifications to the substituents of imine group result in dramatic changes to the productivity and physical properties of the resultant polyolefins [7,8]. Attracted by academic research and potential industrial application, nickel complexes containing pyridylimine ligands were explored for ethylene oligomerization and polymerization [9]. Recently, extensive study have been done with nickel complexes bearing 8-iminoquinoline [10] and related ligands 2-(2-pyridyl)quinoxaline [11] and benzodiazepine [12], these nickel complex systems performed activity for ethylene oligomerization. In our current research, the ligand moiety is modified as benzimidazole to form their nickel complexes, and catalytic behavior of nickel complexes are investigated.

The synthetic procedure of ligands (**L1**–**L5**, 2-aryliminobenzimidazole) and their nickel complexes is generally shown in Scheme 1. Ligands were prepared as white or pale yellow solid in good yields by the condensation of one equivalent of the appropriate aniline with one equivalent of 2-acetylbenzimidazole. Ligands were characterized by microanalysis, ^{1}H NMR and IR spectroscopy. Nickel complexes **1**–**5** [1] were synthesized by dissolving (1,2-dimethoxyethane)nickel bromide in dichloromethane (Scheme 1), followed by addition of two equivalents of the corresponding ligand. The resultant nickel complexes were precipitated from the reaction solution. After washing with diethyl ether and re-crystallized from ethanol, the complexes were obtained in good yield and high purity. The complexes were characterized by elemental analysis, and IR spectroscopy.

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[1] The synthetic details of ligands and the complexes are available in the supplementary material.

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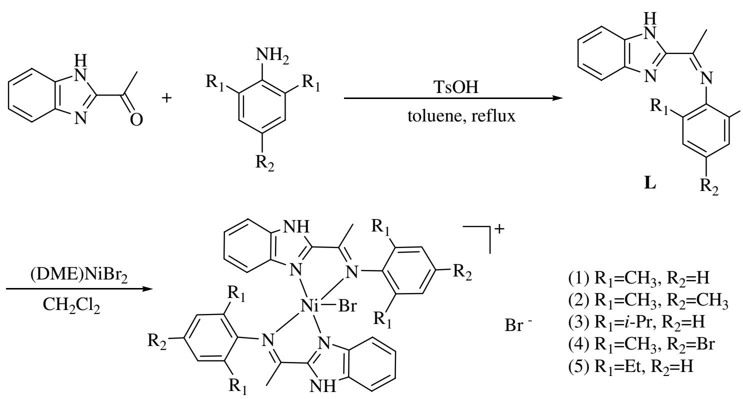

Scheme 1. Synthesis of ligands and complexes.

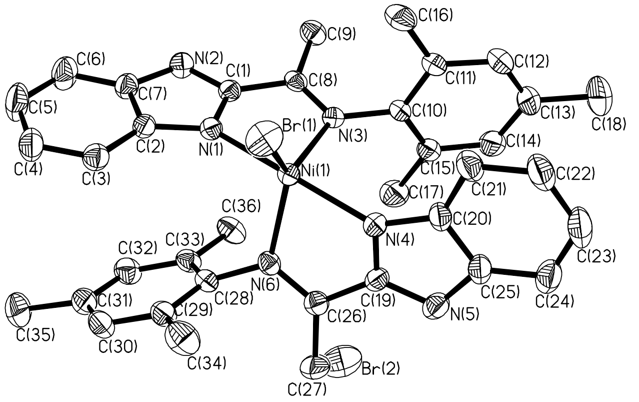

Fig. 1. Crystal structure of complex **2** with 30% probability displacement ellipsoids, H atoms and non-coordinated EtOH molecular are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni(1)–N(4), 2.036(4); Ni(1)–N(1), 2.037(4); Ni(1)–N(6), 2.083(3); Ni(1)–N(3), 2.121(4); Ni(1)–Br(1), 2.3968(11) and N(4)–Ni(1)–N(6), 79.30(14); N(1)–Ni(1)-N(3), 78.96(14); N(1)–Ni(1)–Br(1), 95.65(10); N(3)–Ni(1)–Br(1), 125.64(9); N(4)–Ni(1)–Br(1), 96.55(11); N(6)–Ni(1)–Br(1), 127.60(11).

To confirm its structure, crystal of complex **2** [2] suitable for X-ray determination was grown by vapor diffusion of Et$_2$O into the ethanol solution. The crystal structure of **2** consists of mononuclear complex [Ni(L2)$_2$Br]$^+$Br$^-$ and EtOH solvent molecule (Fig. 1 and Fig. 2). The structure reveals electrostatic interaction between cation complex [Ni(L2)$_2$Br]$^+$ and counterion Br$^-$ (Fig. 2). Each Ni atom locates in an extremely distorted square-pyramidal environment formed by two benzimidazole nitrogen atoms, two imino nitrogen atoms of two ligands and one bromide atom, another bromide atom acting as a counter ion locating far from the center atom Ni(II) [Ni(1)···Br(2) = 6.82 Å]. In the complex, the Ni–N (benzimidazole) [2.036, 2.037 Å] bonds are shorter than the Ni–N (imino) [2.083, 2.121 Å] bonds. Center atom Ni forms two five-membered rings with two ligands, and the two planes [Ni(1)–N(1)–N(3), Ni(1)–N(4)–N(6)] make a dihedral angel of 106.8°. At the same time, the two 2,4,6-trimethyl substituted aryl rings are oriented approximately perpendicular to the their basal coordination plane, with an approximately 89.1° and 92.6° twist angle about the C–N bonds. The non-coordinated EtOH solvent molecule is connected to one **L2** ligand by H-bonding with O1···N5 distance of 2.76 Å.

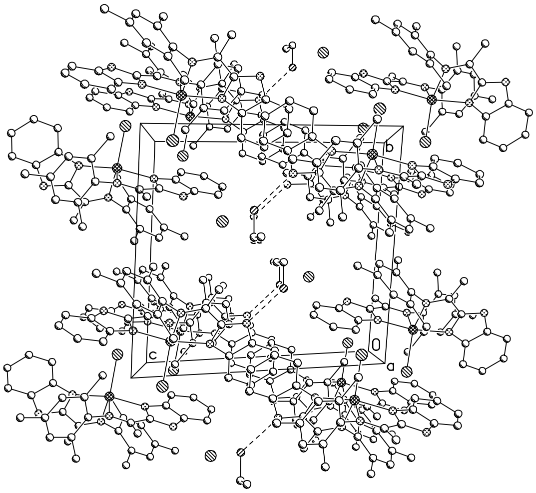

Fig. 2. Packing view along *a*-axis of complex **2**.

Upon treatment with methylaluminoxane (MAO), all of the complexes are active ethylene oligomerization catalysts. The catalysts activity is listed in Table 1, the molecular weight distribution of the oligomers are calculated on the base of GC analysis. Further investigation of complex **2** is performed at different reaction temperatures. Like the complexes in the 8-iminoquinoline [10] and 2-(2-pyridyl)quinoxaline [11] systems, the catalytic activity of complex **2** is sensitive to reaction temperature. Lower temperature is generally favorable, the best

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[2] Complex **2**, [C$_{38}$H$_{44}$Br$_2$N$_6$NiO], $M = 819.32$, triclinic, $P\bar{1}$, $T = 293(2)$ K, $a = 11.921(4)$, $b = 12.899(4)$, $c = 14.313(5)$ Å, $\alpha = 88.475(5)$, $\beta = 66.920(5)$, $\gamma = 75.405(6)°$, $V = 1952.8(11)$ Å^3, $Z = 2$, Number of collected reflections = 11,166, Number of independed reflections = 7823, $R(F^2) = 0.0543$, $wR = 0.1496$. Full crystallographic detail was deposited at the Cambridge Crystallographic Data Center with number CCDC 256208.

Table 1
Activity and distribution for the oligomerization

Cat.	Temp. (°C)	Activity g/mol h atm	Distribution of oligomers (%)							
			C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
1	15	2.11×10^5	6.34	19.07	16.30	23.32	18.95	11.78	3.78	0.73
2	0	1.45×10^5	0.53	13.93	16.14	23.03	17.19	12.99	7.80	3.62
2	15	1.99×10^5	2.07	15.84	14.29	24.79	19.15	13.17	6.43	3.20
2	50	0.72×10^5	18.40	19.54	14.84	21.08	16.24	7.29	1.88	0.74
3	15	1.95×10^5	13.77	17.79	11.54	21.10	18.14	11.85	3.21	1.54
4	15	2.35×10^5	7.99	18.72	14.61	24.48	18.79	11.87	3.26	0.28
5	15	1.86×10^5	12.44	18.60	13.16	23.09	19.15	7.86	3.58	1.22

Condition: catalyst 5 μmol, [Al]/[Ni] = 1500, toluene solvent, 1 atm of ethylene, reaction time 0.5 h.

catalytic temperature is at 15 °C. Steric and electronic environmental around the central metal affects the catalytic activities and the distribution of oligomers. According to Table 1, the order of their activities are listed as 4 > 1 > 2 > 3 > 5 at the same reaction condition. Complex **4** shows the highest activity of 2.35×10^5 g (ethylene) mol^{-1} (Ni) h^{-1}. The oligomers are mixture of α-olefin and internal olefin in range of C_4 to C_{18}. Further detail investigation, including varying reaction conditions and modifying the ligands, is under way.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.inoche.2004.12.021.

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