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Synthesis and characterization of 2-imino-indole nickel complexes and their ethylene oligomerization study

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Abstract

A series of 2-imino-indole derivatives and their neutral nickel complexes were synthesized and characterized. A single-crystal X-ray analysis of $[Ni(C_{10}H_7)(C_{18}H_{16}ClN_2)(PPh_3)]$ shows the nickel center adopted a square-planar coordination geometry. The nickel complexes act solely as effective catalysts for ethylene oligomerization with the activity up to 2.05×10^4 g ethylene mol⁻¹ h⁻¹. © 2003 Elsevier B.V. All rights reserved.

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There has been an increasing interest in the development of late-metal complexes as catalysts for ethylene polymerization or oligomerization under moderate conditions [1,2]. The significant notable are Ni(II)- and Pd(II)-based Brookhard cationic catalysts [ArN = $C(R)C(R) = NAr MCH_3^+$ with bulky substituents on the diimine ligands, as well as numerous late-metal complexes as catalytic precursors [3,4]. Extensively neutral nickel complexes had been developed by DuPont company [5] and Grubbs group [6] based upon the salicylaldiminato ligands. By placing bulky groups to the ortho position of phenoxy, Grubbs reported the salicylaldiminato catalysts could proceed polymerization without additional activator [6] and showed interesting properties for copolymerization [7]. Back to 1980s, ylide-nickel catalysts already showed good activities for ethylene polymerization without cocatalysts [8]. Considering to the industrial application and environmental friendship, the single-component catalyst without adding cocatalyst has gained great attentions. Several series of nickel catalysts for ethylene activities have been investigated in our group [9]. However, none of them could perform ethylene activity without cocatalyst. Herein we demonstrate the new neutral nickel complexes containing 2-*N*-iminoindolyl lignads are capable of ethylene oligomerization without cocatalyst.

The synthetic procedure of ligands (L, 2-imino-3-chloro-1H-indole derivatives) and their neutral nickel complexes is generally shown in Scheme 1. Ligands L were prepared in good yields (65–81%) by the condensation reaction of one equivalent of the appropriate aniline with one equivalent of 3-chloro-1H-indole-2-carboxaldehyde [10], yielding pale yellow crystalline products after purified through re-crystallization in ethanol. Complexes $1-6^{-1}$ were synthesized in reasonable

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¹ Elemental analyses and IR spectra for complexes **1–6**. **1**: $C_{49}H_{44}ClN_2NiP$ Calc. (found): C, 74.88 (74.57); H, 5.64 (5.71); N, 3.56 (3.48). IR(cm⁻¹, KBr): 3227, 1587. **2**: $C_{45}H_{36}ClN_2NiP$ Calc. (found): C, 74.05 (73.90); H, 4.97 (4.82); N, 3.84 (3.96). IR(cm⁻¹, KBr): 1582. **3**: $C_{46}H_{38}ClN_2NiP$ · THF Calc. (found): C, 73.96 (73.59); H, 5.21(5.09); N, 3.45(3.66.). IR(cm⁻¹, KBr): 1585. **4**: $C_{47}H_{40}ClN_2NiP$ Calc. (found): C, 74.48 (74.39); H, 5.32 (5.26); N, 3.70 (3.82). IR(cm⁻¹, KBr): 1588. **5**: $C_{43}H_{31}ClN_3NiO_2P.0.5H_2O$ Calc. (found): C, 68.33 (68.35); H, 4.27 (4.55); N, 5.56 (5.45). IR(cm⁻¹, KBr): 1567. **6**: $C_{43}H_{29}ClF_3N_2NiP$ Calc. (found): C, 68.33 (68.20); H, 3.87 (3.76); N, 3.71 (3.85). IR(cm⁻¹, KBr): 1581. The synthetic details of ligands and the complexes are available in the supplementary materials.



Scheme 1. Synthesis of complexes (isolated yield). Reagents and conditions: (i) EtOH, p-TsOH; (ii) THF, NaH, C₁₀H₇NiCl(PPh₃)₂.



Fig. 1. Crystal structure of complex **3**, 30% probability ellipsoids, H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–C34 1.890(6), Ni1–N2 2.003(3), Ni1–N1 1.984(3), Ni1–P1 2.1652(15), C34–Ni1–N1 168.6(3), N1–Ni1–N2 83.01(15), N1–Ni1–P1 102.40(11), C34–Ni1–N2 90.37(19), C34–Ni1–P1 84.37(16), N2–Ni1– P1 174.56(12).

yields (60–78%) by deprotonation of L with NaH in THF and then reacted with $C_{10}H_7NiCl(PPh_3)_2$ [11]. The resulting solutions were dried under vacuum, and the formed complexes were re-crystallized in diethyl ether. Complexes **1–6** are air-stable solids, and soluble in most organic solvents, such as diethyl ether, CH_2Cl_2 , ethanol, $CHCl_3$ and acetonitrile. The complexes obtained were fully characterized by IR spectra and elemental analysis.

To confirm their structure, complex 3^2 was subjected to single-crystal X-ray diffraction study (Fig. 1). The nickel atom adopts a square-planar coordination geometry. The bulky 2,4,6-trimethylanil occupies the po-

Table 1 The activity of complexes and distribution of oligomers

Catalyst		Temperature (°C)	Activity ^a	Distribution of the oligomers. (%)	
Complex	(µmol)			C_4	C ₆
1	5	80	0.28	32.31	67.69
2	5	15	0.50	85.20	14.80
2	5	40	0.80	56.76	43.24
2	5	60	0.84	85.77	14.23
2	5	80	0.99	91.00	9.00
3	5	40	0.77	81.20	18.80
3	5	60	0.94	86.00	14.00
3	5	80	1.20	88.20	11.80
4	5	80	0.72	77.30	22.7
5	5	80	2.05	79.75	20.25
6	5	80	0.42	72.83	27.17

Toluene solvent, 1 atm of ethylene, reaction time 1 h. $^a \times 10^4 \mbox{ g mol}^{-1} \mbox{ h}^{-1}.$

sition *trans* to the triphenylphosphine ligand with a nearly linear P1–Ni1–N2 angle $(174.56(12)^{\circ})$. The naphthyl group lays *trans* to N1 with an N1–Ni1–C34 angle of 168.6(3)°. The Ni1–P1 bond of **3** (2.1652(15) Å) is similar to that of reported nickel complexes [6]. The Ni–N bonds are slightly different due to nitrogen atoms of aryl ring and imide, the Ni1–N2 bond (2.003(3) Å) is 0.02 Å longer than the Ni1–N1 bond (1.984(3) Å).

It is noteworthy that complexes 1-6 are active for ethylene oligomerization without additional activator. Catalyst activities are calculated on the base of GC analysis, and their activities and oligomers' distributions are listed in Table 1. It is notable of the activity decreasing during the oligomerization reaction, and the final activity is only 10–15% of its beginning value in one hour oligomerization under a constant pressure of one atmosphere of ethylene. The nature of the ligand has a major influence on the catalytic activity. Seen from the Table 1, the order of their activities is listed as 5 > 3 > 2 > 4 > 6 > 1. The higher reaction temperature (~80 °C) is the better catalytic activity appears. At this

² Complex **3**: $C_{40}H_{40}ClN_2NiP$, M = 673.87, triclinic, a = 9.260(2), b = 9.517(2), c = 21.916(4) Å, $\alpha = 99.37(3)$, $\beta = 97.81(3)$, $\gamma = 98.20(3)^\circ$, V = 1860.9(7) Å³, T = 123(2) K, Space group P - 1, Z = 2, Number of collected reflections = 7882, Number of independent reflections = 2332, $R(F^2) = 0.0568$, wR = 0.0652. Full crystallographic detail was deposited at the Cambridge Crystallographic Data Centre with number CCDC 213625.

moment, the activity of complex **5** was obtained with a moderate activity of 2.05×10^4 g mol⁻¹ h⁻¹, which leads to oligomerize ethylene without additional cocatalyst. Further detail investigation, including varying reaction conditions and modifying coordinational ligands, is under way.

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