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Synthesis, molecular structures and norbornene addition polymerization activity of the neutral nickel catalysts supported by *N*-naphthyl-salicylaldiminato ligands

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Abstract

A series of nickel Schiff-base complexes were synthesized by the reaction of Schiff-bases containing *N*-naphththyl group with *trans*-[Ni(PPh₃)₂(Ph)Cl] and they were characterized by EA, IR and NMR. When activated by methylaluminoxane, these complexes exhibit good catalytic activity for the addition polymerization of norbornene. © 2004 Elsevier B.V. All rights reserved.

Keywords: Nickel; Catalysts; Molecular structure; Polymerization; Polynorbornene

Late transition metal catalysts have been one of the most exciting developments in the area of catalysis, organometallic chemistry, and polymer science in recent years [1]. Ni-based catalyst was best known to oligomerize ethylene and dimerize propylene and higher α -olefins because nickel metal was usually thought to generally prefer β -hydride elimination followed by reductive elimination before 1995 [2], however, the discovery of salicylaldiminato nickel complexes as high active catalysts for polymerization of olefin has become a great break-through [3].

During the past few years, most of our effort has focused on neutral, single-component nickel ethylenepolymerization catalysts before we began our cyclo-olefins polymerization study. Several series of nickel catalysts supported by [**N**, **O**] mono-anionic and bisanionic ligands, including salicylaldiminato phenyl

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nickel complexes [4] and binuclear 2,5-disubstitutedamino-p-benzoquinone nickel(II) complexes [5], were designed and synthesized on the basis of recent developments. And these neutral nickel complexes based on anion ligands are very reactive toward ethylene. Deming and Novak [6] introduced the first nickel complexes for the addition polymerization of norbornene in 1993 and recently several other catalyst systems are presented [7]. This paper aims to investigate what effect can be brought in by replacement of the phenyl with naphthyl group in the imino moiety of salicylaldiminato nickel complexes, since the latter has a larger conjugated system (Scheme 1). Polymerizations of norbornene were carried out with these complexes as catalysts in the presence of methylaluminoxane as a co-catalyst.

The complexes were prepared as shown in Scheme 1, including 4e to make comparison, the preparation procedures were according to the analogous method of reference [3b]. All complexes were characterized by EA, IR and ¹H NMR [8]. In the IR spectra of complexes, the

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b: R_1 =t-Bu, R_2 =H, Ar=Naphthyl c: R_1 =H, R_2 =OCH₃, Ar=Naphthyl d: R_1 =NO₂, R_2 =NO₂, Ar=Naphthyl e: R_1 =H, R_2 =H, Ar=Phenyl







Fig. 1. Molecular structure of complex **4a**. Selected bond lengths (Å) and angles (°): Ni(1)–O(1) 1.8808(17), Ni(1)–C(19) 1.892(2), Ni(1)–N(1) 1.937(2), Ni(1)–P(1) 2.1696(10), N(1)–C(35) 1.292(3) and O(1)–Ni(1)–C(19) 176.60(9), O(1)–Ni(1)–N(1) 91.59(8), C(19)–Ni(1)–N(1) 91.73(9), O(1)–Ni(1)–P(1) 91.10(6), C(19)–Ni(1)–P(1) 85.57(7), N(1)–Ni(1)–P(1) 177.15(6).

bands of C=N are shifted to lower frequencies for different amounts, respectively, due to the coordination between azomethine nitrogen and nickel.

Fig. 2. Molecular structure of complex **4c**. Selected bond lengths (Å) and angles (°): Ni(1)–C(19) 1.887(4), Ni(1)–O(1) 1.896(3), Ni(1)–N(1) 1.946(3), Ni(1)–P(1) 2.184(2), N(1)–C(35) 1.288(4) and C(19)–Ni(1)–O(1) 175.13(13), C(19)–Ni(1)–N(1) 90.33(13), O(1)–Ni(1)–N(1) 91.60(11), C(19)–Ni(1)–P(1) 85.32(11), O(1)–Ni(1)–P(1) 93.12(9), N(1)–Ni(1)–P(1) 173.50(8).

The ORTEP diagrams of **4a** and **4c** are shown in Figs. 1 and 2, respectively [9], along with selected bond lengths and angles.

Table 1 Results of norbornene polymerization initiated by catalysts **4a**–e

Run	Cat	<i>T</i> (°C)	Yield (%)	Activity (g-PNB/mol-Ni · h)	$M_{\rm v}$ (g/mol)	$M_{\rm n}^{\rm b}$ (g/mol)	$M_{\rm w}/M_{\rm n}^{\rm b}$
1	4b	0	39.25	2.22×10^{7}	1.19×10^{5a}		
2	4b	15	46.31	2.62×10^{7}	1.37×10^{6a}		
3	4b	30	65.06	3.68×10^{7}	2.58×10^{6b}	1.07×10^{6}	2.72
4	4b	45	60.81	3.44×10^{7}	4.70×10^{5a}		
5	4b	60	64.21	3.63×10^{7}	4.06×10^{5a}		
6	4 a	30	60.38	3.41×10^{7}	2.17×10^{6b}	7.77×10^{5}	3.22
7	4c	30	56.35	3.18×10^{7}	2.63×10^{6b}	1.07×10^{6}	2.79
8	4d	30	67.50	3.81×10^{7}	1.95×10^{6b}	5.98×10^{5}	3.81
9	4 e	30	29.63	1.67×10^{7}	$2.06\times10^{6\mathrm{b}}$	7.71×10^{5}	3.05

Polymerization conditions: reaction volume: 15 ml; time: 10 min; solvent: chlorobenzene; [Al]/[Ni] = 2665; $[Ni] = 1.33 \times 10^{-5} \text{ mol/l}$; [NBE]/[Ni] = 100 000.

^a Obtained by capillary viscosimetry using the Mark–Houwink coefficients: $\alpha = 0.56$, $K = 7.78 \times 10^{-4}$ dl/g [11a].

^b Obtained by GPC [11b].

The molecule of **4a** adopts a nearly ideal square-planar coordination geometry with the Ni approximately 0.091 Å out of the plane of its ligands. The 1-naphthylimido-group occupies the position *trans* to the triphenylphosphine ligand with a nearly linear N(1)–Ni–P(1) angle (177.15(6)°). The Ni(1)–P(1) bond distance (2.1696(10) Å) is between that in Grubbs' nickel-based complex (d(Ni–P) 2.172(2) Å) and that in Cavell's [Ni(P-Ph₃)(*o*-tolyl)(N–O)] complex with N–O bidentate pyridinecarboxylate ligand (d(Ni–P) 2.1653(2) Å) [3b,10].

The coordination sphere of complex **4c** was found to be alike (Fig. 2), the Ni(1), N(1), O(1), P(1), C(19) atoms are coplanar (mean deviation, 0.0636 Å). One benzene molecule is incorporated in a unit cell.

The catalyst of **4b** showed quite good activities over a wide range (0–60 °C) of reaction temperature, the activity increased with higher temperature and reached a plateau around 30 °C. Except for 0 °C, the molecular weight of the obtained polymer declined with higher temperature. The reason for this exception might be plausibly attributed to that under low temperature, the propogation of the polymer chain could not be fully developed in 10 min (see Table 1).

The structures of the neutral Ni(II) complexes clearly affected the activities. Since naphthyl group is a two-ring conjugated system while phenyl is a one-ring conjugated system, replacement of phenyl with naphthyl in the molecule might bring an electron property modification to the complex. All of **4a–d** showed a higher activity roughly doubled that of **4e**. The resulted polymers are soluble in chlorobenzene at room temperature. Although different molecular weights were obtained by changing reaction conditions, same spectra were observed for those polynorbornenes [12].

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[8] To a stirred solution of salicylaldehyde (26.8 mmol) in dried ethanol (40 ml), 1-naphthylamine (4.32 g, 30.2 mmol) and formic acid (0.5 ml) were added. The reaction mixture was stirred for 24 h at room temperature. Subsequently, the solution was concentrated and the brown precipitate was separated by filtration, then purified with column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1) to afford 2a as yellow solid (4.19 g). The other ligands were prepared by similar procedures, except for that they were refluxed for 2 h instead of stirred for 24 h at room temperature. 2a (63.2% yield). ¹H NMR (500 MHz, CDCl₃): δ 6.98–8.25 (m, 11H, aromatic-H), 8.70 (s, 1H, CH=N), 13.37 (s, 1H, OH). IR (KBr pellet, v (cm⁻¹)): 1621.8 (s). Anal. Calc. for C₁₇H₁₃NO: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.66; H, 5.30; N, 5.60. **2b** (73.3% yield). ¹H NMR (500 MHz, CDCl₃): δ 1.52 (s, 9H, t-Bu), 6.91-8.30 (m, 10H, aromatic-H), 8.72 (s, 1H, CH=N), 13.92 (s, 1H, OH). IR (KBr pellet, v (cm⁻¹)): 1606.0 (s). Anal. Calc. for C21H21NO: C, 83.14; H, 6.98; N, 4.61. Found: C, 83.14; H, 7.05; N, 4.72. 2c (68.8% yield). ¹H NMR (400 MHz, CDCl₃): δ 3.78 (s, 3H, OCH₃), 6.97–8.19 (m, 10H, aromatic-H), 9.00 (s, 1H, CH=N), 12.41 (s, 1H, OH). IR (KBr pellet, v (cm⁻¹)): 1618.9 (s). Anal. Calc. for $C_{18}H_{15}NO_2\!\!:C,\,77.96;\,H,\,5.45;\,N,\,5.04.$ Found: C, 77.77; H, 5.41; N, 4.79. 2d (74.2% yield). ¹H NMR (400 MHz, DMSO): *δ* 6.95–8.18 (m, 7H, naphthyl-H), 8.87 (s, 1H, subst. phenyl-H), 8.92 (s, 1H, subst. phenyl-H), 9.68 (s, 1H, CH=N), 2.8-4.2 (br, exchangeable with D₂O). IR (KBr pellet, v (cm^{-1}) : 1620.4 (s). Anal. Calc. for $C_{17}H_{11}N_3O_5$: C, 60.55; H, 3.29; N, 12.44. Found: C, 60.62; H, 3.25; N, 12.51.A solution of ligand 2a (0.495 g, 2 mmol) in THF (20 ml) was added to excess amount of NaH. The resulting mixture was stirred at room temperature for 2 h, then filtered. And the filtrate was evaporated. The greenish-yellow residue was washed with hexane (20 ml) and dried in vacuum, yielding the Na salt 3a as yellow powder. The Na salt 3a (0.295 g, 1.097 mmol) and trans-[Ni(PPh₃)₂(Ph)Cl] (0.733 g, 1.053 mmol) were jointed together in a Schlenk flask, 20 ml of benzene was added, then stirred at room temperature for 8 h. The reaction mixture was filtered by cannula filtration, and the filtrate was concentrated in vacuo to ca. 5 ml. Then 30 ml of hexane was added and a yellow-orange solid precipitated from solution and was isolated by cannula filtration, then washed several times with hexane to yield 0.608 g (0.944 mmol) of 4a. The other nickel complexes 4b-e were prepared by analogous procedures. 4a (89.6% yield). ¹H NMR (500 MHz, CDCl₃): δ 5.45-8.25 (m,31H, aromatic-H), 8.62 (s, 1H, CH=N). IR (KBr pellet, v (cm⁻¹)): 1605.1 (s). Anal. Calc. for C₄₁H₃₂NOPNi: C, 76.42; H, 5.01; N, 2.17. Found: C, 76.15; H, 4.89; N, 2.13. 4b (68.2% yield). ¹H NMR

(400 MHz, CDCl₃): δ 2.17 (s, 9H, t-Bu), 5.30-8.35 (m, 30H, aromatic-H), 8.58 (s, 1H, CH=N). IR (KBr pellet, v (cm⁻¹)): 1583.5 (s). Anal. Calc. for C45H40NOPNi: C, 77.16; H, 5.76; N, 2.00. Found: C, 77.26; H, 5.79; N, 2.10. 4c (66.7% yield). ¹H NMR (400 MHz, CDCl₃): δ 3.69 (s, 3H, OCH₃), 5.48-8.28 (m, 30H, aromatic-H), 8.63 (s, 1H, CH=N). IR (KBr pellet, v (cm⁻¹)): 1615.4 (s). Anal. Calc. for C42H34NO2PNi · 1/2C6H6: C, 75.76; H, 5.23; N, 1.96. Found: C, 75.44; H, 5.21; N, 1.50. 4d (70.8% yield). ¹H NMR (400 MHz, CDCl₃): δ 5.53-8.34 (m, 29H, aromatic-H), 8.60 (s, 1H CH=N). IR (KBr pellet, v (cm⁻¹)): 1615.5(s). Anal. Calc. for C41H30N3O5PNi: C, 67.06; H, 4.12; N, 5.72. Found: C, 67.19; H, 4.15; N, 5.56. 4e (80.8% yield). ¹H NMR (400 MHz, CDCl₃): δ 5.60–8.10 (m, 29H, aromatic-H), 8.64 (s, 1H, CH=N). IR (KBr pellet, v (cm⁻¹)): 1610.2 (s). Anal. Calc. for C₃₇H₃₀NOP-Ni · 1/2C₆H₆: C, 75.86; H, 5.25; N, 2.21. Found: C, 75.93; H, 5.71; N. 2.43.

- [9] Crystal data for 4a: C₄₁ H₃₂NNiOP, $M_r = 644.36$, Triclinic, $P\bar{1}$ $a = 10.633(4), b = 11.405(4), c = 14.924(5) \text{ Å}, \alpha = 69.687(4)^{\circ},$ $\beta = 70.648(4)^{\circ}, \quad \sigma = 83.103(4)^{\circ}, \quad V = 1601.2(9) \quad \text{Å}^3, \quad Z = 2,$ F(000) = 672, $D_{calc} = 1.336 \text{ g cm}^{-3}$, Of 7231 data collected, 6082 were unique. [$R_{int} = 0.0158$]. Final R indices [$I > 2\sigma(I)$], $R_1 = 0.0396$, $wR_2 = 0.0904$. Crystal data for **4c**: C₄₅H₃₇NNiO₂P, $M_{\rm r} = 713.44$, Triclinic, $P\bar{1}$, a = 11.386(13), b = 13.215(14), c =13.971(16) Å, $\alpha = 65.645(15)^\circ$, $\beta = 70.681(15)^\circ$, $\lambda = 87.220(16)^\circ$, V = 1798(3) Å³, Z = 2, F(000) = 746, $D_{calc} = 1.318$ g cm⁻³, of 7618 data collected, 6245 were unique. [$R_{int} = 0.0217$]. Final R indices $[I > 2\sigma(I)]$, $R_1 = 0.0492$, $wR_2 = 0.1040$. All the data were collected on a CCD-Bruker Smart diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at room temperature using the ω scan technique. The structures were solved by the direct method, expanded using Fourier techniques and refined on F^2 by a full-matrix least-squares method. Anisotropic displacement parameters were included for all non-hydrogen atoms. All the calculations were carried out with Siemens SHELXTL PLUS program. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center CCDC Nos. 248435 and 248436.
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- [12] Spectra of the resulted polynorbornenes: IR (KBr pellet, ν (cm⁻¹)): 2944.6 (vs), 2867.6 (vs), 1474.4 (m), 1453.0 (s), 1294.1 (m). ¹H NMR (*o*-dichlorobenzene-*d*4): $\delta = 1.0-2.7$ ppm (m, maxima at 1.31, 1.55, 1.71, 2.46). ¹³C NMR (*o*-dichlorobenzene-*d*4): $\delta = 29-52$ ppm (m, maxima at 31.1, 38.1, 47.1).