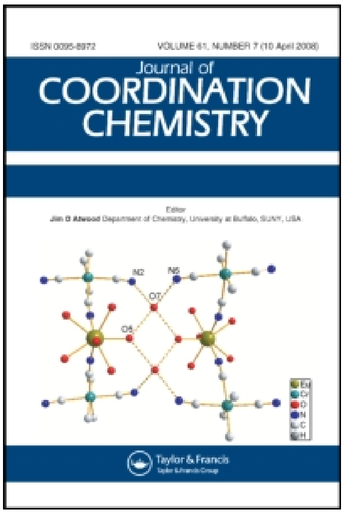

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, structure and olefin polymerization catalysis of nickel(II) complexes bearing N,O-chelate ligands

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To cite this Article Gui, Guoqiu , Bao, Feng , Gao, Haiyang , Zhu, Fangming and Wu, Qing(2006) 'Synthesis, structure and olefin polymerization catalysis of nickel(II) complexes bearing N,O-chelate ligands', Journal of Coordination Chemistry, 59: 1, 107 — 118

To link to this Article: DOI: 10.1080/00958970500364043

URL: http://dx.doi.org/10.1080/00958970500364043

Journal of Coordination Chemistry
Vol. 59, No. 1, January 2006, 107–118

Synthesis, structure and olefin polymerization catalysis of nickel(II) complexes bearing N,O-chelate ligands

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(*Received 21 February 2005; in final form 18 April 2005*)

Four β-ketoimine ligands (two series) were prepared through traditional condensation reactions of β-diketones with 2,6-substituted anilines. Reaction took place only at the cyclohexanone carbonyl rather than at the acetyl or benzoyl carbonyl, even if more than two equivalents of the amines were added. Consequently, four new moisture- and air-stable bis(β-ketoamino)nickel(II) complexes, Ni[2–$CH_3C(O)C_6H_8$(=NAr)]$_2$ (Ar = 2, 6-$iPr_2C_6H_3$, (**1**); Ar = 2, 6-$Me_2C_6H_3$, (**2**) and Ni[2–PhC(O)C_6H_8(=NAr)]$_2$ (Ar = 2, 6-$iPr_2C_6H_3$, (**3**); Ar = 2, 6-$Me_2C_6H_3$, (**4**) were obtained and characterized. The solid-state structures of complex **1**, **2** and **3** have been determined by single-crystal X-ray diffraction. Additionally, these complexes can be applied as highly active catalyst precursors for vinyl polymerization of norbornene (NBE) after activation with methylaluminoxane (MAO).

Keywords: β-ketoimine; Nickel complex; Olefin polymerization; Norbornene; Vinyl polymerization

1. Introduction

Traditionally, late-metal catalysts were only found to produce dimers or low-molecular-weight oligomers of olefins due to chain termination via β-hydrogen elimination [1–3]. Since Brookhart and co-workers first reported high-activity nickel and palladium olefin polymerization catalysts in 1995 [4], late-metal catalysts for olefin polymerization, because of their lower oxophilicity and resistance toward deactivation by polar functionalities compared with early transition metal counterparts, began to attract renewed attention. As promising alternatives to both traditional Ziegler-Natta [5, 6] and metallocene [7–10] catalysts for the polymerization of olefins, late-metal catalysts which always include the metal complex and a cocatalyst

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Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500364043

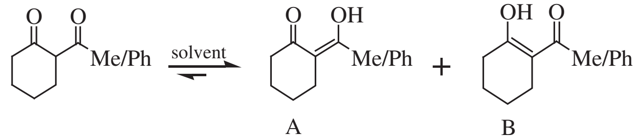
like MAO, are a research focus. Many significant advances, especially involving nickel catalysts, have been made during the last decade [11–19]. Because variation of ligand structure can lead to profound changes in the catalytic activity and the properties of the polymer, efforts have focused on finding new with different donating atoms, such as N, P, O, S, and obtaining new nickel catalyst precursors and controlled synthesis of polyolefin products.

β-ketoimines are common Schiff bases that can be obtained from traditional 1 : 1 (50% mole excess) condensation of a β-diketone with primary amine [20]. These bases have three tautomers (Schiff base, ketamine and enimine), and they can exist in any of three forms. In most solvents, these compounds are completely tautomerized to the ketamine form [21]. As a result, through removing the acid proton with a strong base, like $KOC(CH_3)_3$, metal complexes bearing β-ketoamino ligands, including bis(β-ketoamino)nickel(II) complexes, bis(β-ketoamino)cobalt(II) complexes, have been prepared and studied [22–26]. Recently, bis(β-ketoamino)nickel(II) complexes have sparked new interest in developing late-metal catalysts for olefin polymerization. Bis(β-ketoamino)nickel(II) complexes prepared through $KOC(CH_3)_3$ deprotonation, which can serve as active catalyst precursors for methyl methacrylate (MMA) polymerization, were reported [27]. Related nickel complexes prepared with NaH, were active precatalysts for norbornene (NBE) polymerization [28]. In order to better understand such nickel complexes, we have designed new nonsymmetric bidentate β-ketoimine ligands, to transform to the desired anionic [N, O] chelate complex with a 2,6-substituted *N*-aryl group. With another strong base, n-BuLi, here we report the synthesis, structure and olefin polymerization behavior of the new nickel(II) complexes with β-ketoamino ligands.

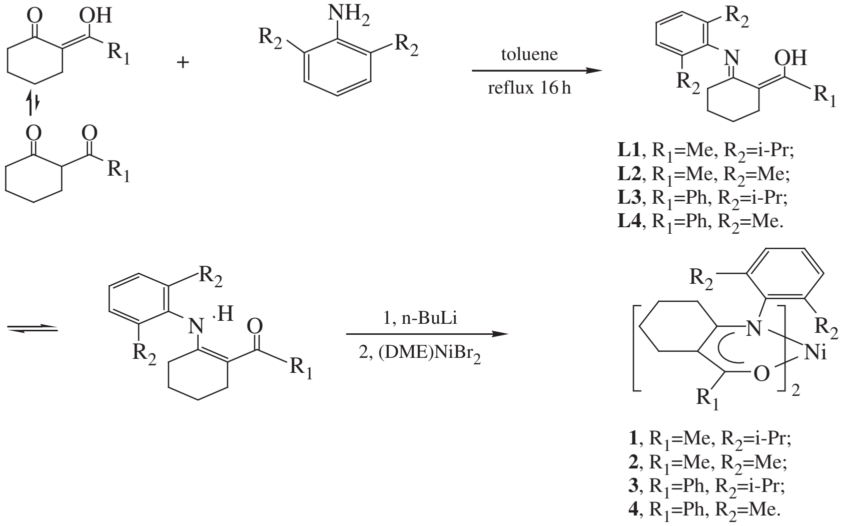
2. Results and discussion

2.1. *β-ketoimine ligands and bis(β-ketoamino)nickel(II) syntheses*

Four *N*-aryl-substituted β-ketoimine ligands, 2-(2,6-diisopropylphenyl)amino-1-cyclohexyl methyl ketone (**L1**), 2-(2,6-dimethylphenyl)amino-1-cyclohexyl methyl ketone (**L2**), 2-(2,6-diisopropylphenyl)amino-1-cyclohexyl phenyl ketone (**L3**) and 2-(2,6-dimethylphenyl)amino-1-cyclohexyl phenyl ketone (**L4**) were synthesized by condensation of the corresponding 1,3-diketones and anilines in a 1 : 1 molar ratio by refluxing in toluene with removal of water. When the molar ratio of the diketone to the primary amine was changed from 1 : 1 to 1 : 2 or even 1 : 3, we could not obtain the expected β-diimine ligands. The final compounds still were the same β-ketoimine ligands, similar to other diketones [29]. Condensation only occurs at the cyclohexanone carbonyl rather than at the acetyl or benzoyl carbonyl due to steric hindrance. Given the well-known keto-enol tautomerism, most β-diketones transform easily to enols in solution. Here, the 1,3-diketones can form two enols (see scheme 1), A and B, in acid solution because of the different substituents [30]. Compared with enol A, the steric hindrance of enol B makes it more difficult to obtain nucleophilic addition for the amines of the acetyl or benzoyl carbonyl owing to the methyl or phenyl group. The subsequent reactions of ligands with $(DME)NiBr_2$ (DME = 1,2-dimethoxyethane) in the presence of *n*-BuLi lead to formation of new bis(β-ketoamino)nickel(II) complexes **1**–**4** in high yields (see scheme 2).



Scheme 1. Keto-enol tautomerism of 1, 3-diketones.



Scheme 2. Synthesis route of Ni complexes.

Crystals of complexes **1**, **2** and **3** suitable for single crystal X-ray diffraction analysis were grown from toluene solutions. The molecular structures are shown in figures 1, 2 and 3, respectively. Table 1 lists the selected bond lengths and angles, and the crystallographic data are summarized in table 2. The coordination geometries of three complexes were demonstrated to be very similar in the solid state. The complexes are mononuclear and nearly ideal four-coordinate, square-planar configurations. The formation of tetrahedral complexes, although sterically possible, was not observed. The nickel ion in the three complexes is arranged in a nearly perfect square-planar coordination environment where β-ketoamino acts as a monoanionic bidentate N,O-chelator, and lies in the trans-configuration to create two stable six-membered chelate rings (NiOCCCN).

2.2. *Catalytic olefin polymerization*

Activating these complexes with MAO, we tried to polymerize some common α-olefins, such as ethylene and styrene. Disappointingly, no polymers were obtained, showing these complexes to be inactive for α-olefin polymerization. In contrast, all four complexes can efficiently catalyze NBE polymerization in the presence of MAO. The results of the NBE polymerizations are summarized in table 3. The steric hindrance of the complexes has significant effect on their catalytic activities. The complexes with 2,6-isopropyl-substituted *N*-aryl have higher catalytic activities for the polymerization than the related complexes with 2,6-methyl-substituted *N*-aryl, i.e. **1** > **2** and **3** > **4**,

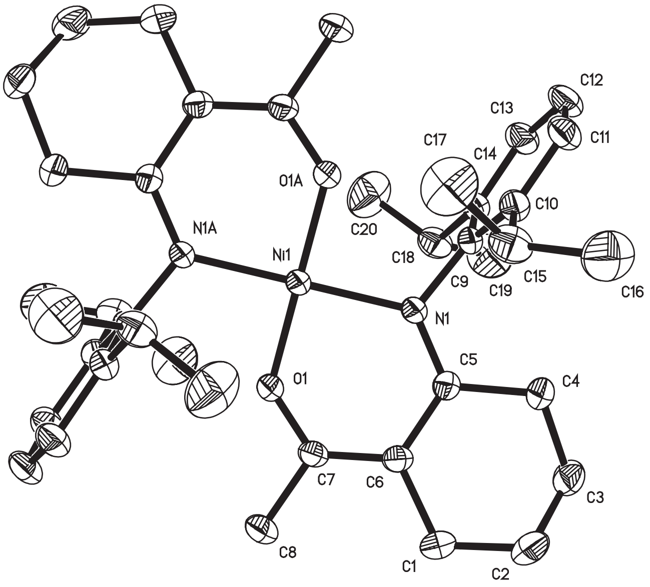


Figure 1. Molecular structure of nickel complex **1**. Thermal ellipsoids at the 50% level are shown. Hydrogen atoms are omitted for clarity.

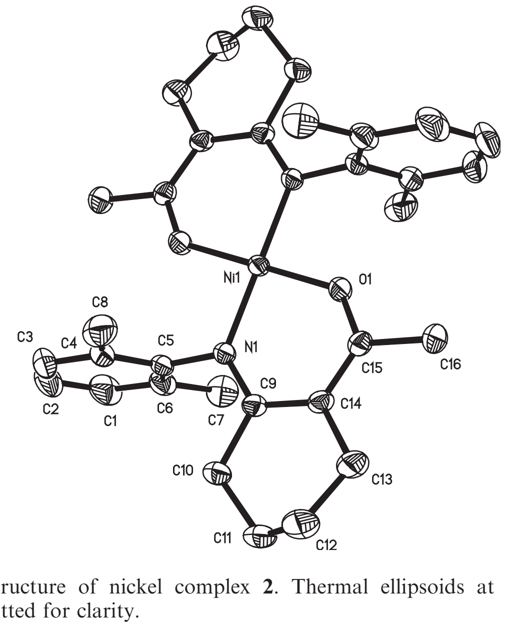


Figure 2. Molecular structure of nickel complex **2**. Thermal ellipsoids at the 50% level are shown. Hydrogen atoms are omitted for clarity.

especially at high temperatures. This fact suggests that the high steric hindrance of the aryl group is favorable for increasing catalytic activity, as for silacylideneimino-based nickel complexes [31]. Additionally, complexes **3** and **4** with benzoyl group are more active than the related complexes **1** and **2** with an acetyl group. More effective conjugation of the benzoyl group may be favorable to stabilizing the insertion transition state

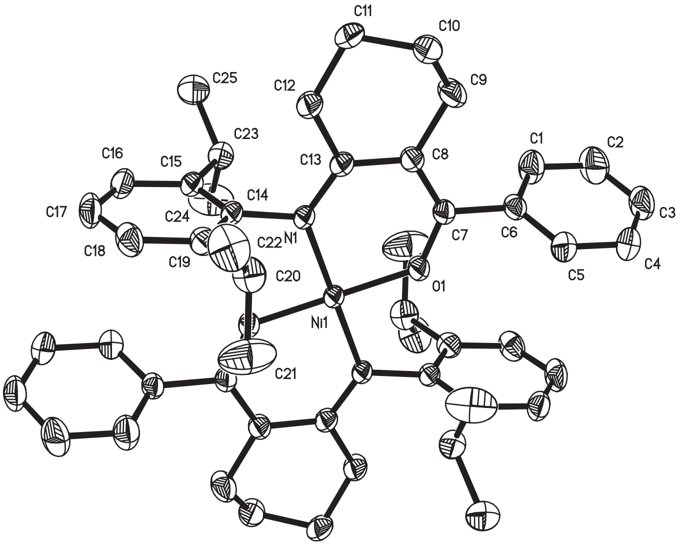


Figure 3. Molecular structure of nickel complex **3**. Thermal ellipsoids at the 50% level are shown. Hydrogen atoms are omitted for clarity.

when the phenyl ring orients itself in a coplanar fashion with the ketoimine chelating ring in the course of propagation, resulting in lowering the propagation barrier [32] and increasing the activity. For all the complexes, with increasing polymerization temperature, the catalytic activity turns higher and the molecular weight of the polymer decreases.

The polynorbornenes (PNBE) afforded by the catalyst systems have high molecular weights from 10^5 to $10^6\,\mathrm{g\,mol^{-1}}$, indicating the polymerization is not a typical cationic or free-radical polymerization, which usually forms low molecular weights (molecular weight <1000) and low yield because of rearrangements and transfer reactions. All the polymers showed very similar FTIR and ^{1}H-NMR spectra (see figures 4 and 5). There were no 1620–1680 $\mathrm{cm^{-1}}$ absorptions in the FTIR spectra, indicating no C=C double bond. ^{1}H-NMR spectra of the PNBE also proved no double bond-H ($\delta > 4$ ppm). These facts show that the norbornene polymerizations catalyzed by the β-ketoamino nickel complexes activated with MAO proceeds through a vinyl-addition polymerization mechanism rather than ring-opening metathesis polymerization (ROMP). In addition, all polymers are soluble in chlorobenzene, *o*-dichlorobenzene and cyclohexane at room temperature, indicating low stereoregularity [33–35].

3. Experimental section

3.1. *General procedures and materials*

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk techniques. Solvents were purified using standard procedures. 2-acetylcyclohexanone, 2-benzoylcyclohexanone, 2,6-dimethylphenylamine, 2,6-diisopropylphenylamine,

Table 1. Selected bond lengths (Å) and angles (°) for complexes **1**, **2** and **3**.

Complex **1**		Complex **2**		Complex **3**	
Ni(1)–O(1)#1	1.8129(11)	Ni(1)–O(1)	1.8127(13)	Ni(1)–O(1)	1.8158(13)
Ni(1)–O(1)	1.8129(11)	Ni(1)–O(1)#1	1.8127(13)	Ni(1)–O(1)#1	1.8158(13)
Ni(1)–N(1)	1.9144(12)	Ni(1)–N(1)#1	1.9145(14)	Ni(1)–N(1)	1.9204(14)
Ni(1)–N(1)#1	1.9144(12)	Ni(1)–N(1)	1.9145(14)	Ni(1)–N(1)#1	1.9205(14)
C(5)–N(1)	1.3283(19)	C(9)–N(1)	1.330(2)	C(13)–N(1)	1.323(2)
C(7)–O(1)	1.282(2)	C(15)–O(1)	1.287(2)	C(7)–O(1)	1.282(2)
C(9)–N(1)	1.4465(17)	C(5)–N(1)	1.442(2)	C(14)–N(1)	1.451(2)
C(1)–C(6)	1.525(2)	C(13)–C(14)	1.524(3)	C(8)–C(9)	1.529(5)
C(1)–C(2)	1.493(4)	C(12B)–C(13)	1.472(16)	C(9)–C(10)	1.511(7)
C(1)–C(2B)	1.541(7)	C(12A)–C(13)	1.504(4)	C(10)–C(11)	1.533(5)
C(2)–C(3)	1.523(4)	C(11B)–C(12B)	1.59(2)	C(11)–C(12)	1.519(6)
C(2B)–C(3B)	1.517(7)	C(11A)–C(12A)	1.504(6)	C(12)–C(13)	1.526(4)
C(3B)–C(4)	1.507(7)	C(10)–C(11A)	1.514(4)	C(12B)–C(13)	1.524(7)
C(3)–C(4)	1.509(3)	C(10)–C(11B)	1.627(12)	C(9B)–C(10B)	1.516(8)
C(4)–C(5)	1.521(2)	C(9)–C(10)	1.518(3	C(10B)–C(11B)	1.535(7)
C(5)–C(6)	1.423(2)	C(9)–C(14)	1.419(3)	C(11B)–C(12B)	1.520(7)
C(6)–C(7)	1.371(2)	C(14)–C(15)	1.374(3)	C(7)–C(8)	1.368(2)
O(1)#1–Ni(1)–O(1)	180.0	O(1)–Ni(1)–O(1)#1	180.0	O(1)–Ni(1)–O(1)#1	180.0
O(1)–Ni(1)–N(1)	91.05(5)	O(1)#1–Ni(1)–N(1)#1	91.43(6)	O(1)–Ni(1)–N(1)	91.50(6)
O(1)–Ni(1)–N(1)#1	88.95(5)	O(1)#1–Ni(1)–N(1)	88.57(6)	O(1)#1–Ni(1)–N(1)	88.51(6)
N(1)–Ni(1)–N(1)#1	180.00(11)	N(1)#1–Ni(1)–N(1)	180.0	N(1)–Ni(1)–N(1)#1	180.0
C(2)–C(1)–C(6)	114.60(19)	C(12A)–C(13)–C(14)	114.5(2)	C(10)–C(9)–C(8)	112.2(5)
C(6)–C(1)–C(2B)	113.8(3)	C(12B)–C(13)–C(14)	114.8(7)	C(9)–C(10)–C(11)	106.3(5)
C(1)–C(2)–C(3)	107.4(3)	C(12A)–C(11A)–C(10)	109.5(3)	C(12)–C(11)–C(10)	109.0(5)
C(4)–C(3)–C(2)	110.9(3)	C(12B)–C(11B)–C(10)	101.6(11)	C(8)–C(13)–C(12B)	118.2(6)
C(3)–C(4)–C(5)	114.81(18)	C(9)–C(10)–C(11B)	108.0(5)	C(11)–C(12)–C(13)	115.8(6)
C(3B)–C(4)–C(5)	115.6(3)	C(11A)–C(10)–C(9)	115.0(2)	C(7)–C(8)–C(9B)	119.3(5)
N(1)–C(5)–C(4)	118.30(13)	N(1)–C(9)–C(10)	117.90(17)	C(8)–C(13)–C(12)	117.4(3)
C(6)–C(5)–C(4)	118.46(14)	C(14)–C(9)–C(10)	118.75(17)	C(7)–C(8)–C(9)	118.2(3)
C(7)–C(6)–C(5)	120.69(14)	C(15)–C(14)–C(9)	121.19(17)	C(7)–C(8)–C(13)	120.85(16)
C(7)–C(6)–C(1)	117.99(15)	C(15)–C(14)–C(13)	117.78(18)	C(10B)–C(9B)–C(8)	113.1(8)
C(5)–C(6)–C(1)	121.24(15)	C(9)–C(14)–C(13)	121.03(18)	C(9B)–C(10B)–C(11B)	102.6(10)
O(1)–C(7)–C(6)	125.85(14)	O(1)–C(15)–C(14)	125.50(18)	C(12B)–C(11B)–C(10B)	104.7(10)
C(5)–N(1)–C(9)	117.60(12)	C(9)–N(1)–C(5)	117.45(15)	C(11B)–C(12B)–C(13)	111.3(8)
C(9)–N(1)–Ni(1)	115.45(9)	C(5)–N(1)–Ni(1)	115.76(11)	C(13)–N(1)–Ni(1)	126.82(11)
C(7)–O(1)–Ni(1)	130.01(11)	C(15)–O(1)–Ni(1)	130.28(14)	C(7)–O(1)–Ni(1)	130.33(11)

Note: Symmetry transformations used to generate equivalent atoms.

MAO solution and *n*-BuLi were bought from Aldrich and used without further purification. (DME)NiBr$_2$ was prepared following the published procedure with minor modification [36]. NBE was purified by drying with potassium at 60°C for 8 h and distilled, then dissolved in toluene to make a 5.0 mol L^{-1} solution. Elemental analyses were performed on a Vario EL microanalyzer. FTIR spectra were recorded on a Nicolet 205 spectrometer (KBr). NMR spectra were carried out on an INOVA 500 Hz at room temperature in CDCl$_3$ solution using TMS as internal standard for ligands and complexes and at 120°C in *o*-C$_6$D$_4$Cl$_2$ for polymer samples. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution of polymers were performed on a Waters Breeze instrument using chlorobenzene as the eluent at 40°C and standard polystyrene as the reference.

3.1.1. [2-CH$_3$C(O)C$_6$H$_9$(=NAr)] (L1, Ar=2,6-^{i}Pr$_2$C$_6$H$_3$). 2-acetylcyclohexanone (3.40 mL, 0.025 mol), 2,6-diisopropylaniline (5.10 mL, 0.025 mol) and a catalytic amount of *p*-toluenesulfonic acid were combined in toluene (50 mL), and the

Table 2. Crystallographic data for complexes **1**, **2** and **3**.

	Complex **1**	Complex **2**	Complex **3**
Empirical formula	$C_{40}H_{56}N_2NiO_2$	$C_{32}H_{40}N_2NiO_2$	$C_{50}H_{60}N_2NiO_2$
Formula weight	655.58	543.37	779.71
Crystal's color	Dark green	Green	Dark green
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2(1)/c$	Triclinic, $P\bar{1}$
Unit cell dimensions (Å, °)	$a = 8.8614(11)$ $b = 10.2035(12)$ $c = 11.3009(14)$ $\alpha = 112.127(2)$ $\beta = 103.297(2)$ $\gamma = 92.874(2)$	$a = 10.8814(14)$ $b = 10.9589(15)$ $c = 15.538(2)$ $\alpha = 90$ $\beta = 130.166(2)$ $\gamma = 90$	$a = 9.854(4)$ $b = 11.039(4)$ $c = 12.033(4)$ $\alpha = 71.920(5)$ $\beta = 68.826(5)$ $\gamma = 63.907(5)$
Volume ($Å^3$)	910.50(19)	1415.9(3)	1078.1(7)
Z, Calculated density ($Mg\,m^{-3}$)	1, 1.196	2, 1.274	1, 1.201
Absorption coefficient (mm^{-1})	0.568	0.716	0.490
$F(000)$	354	580	418
Crystal size (mm)	0.49 × 0.42 × 0.35	0.40 × 0.35 × 0.25	0.46 × 0.30 × 0.15
θ range for data collection (°)	2.02 to 27.08	2.45 to 27.04	1.85 to 27.10
Limiting indices	$-11 \le h \le 11$, $-13 \le k \le 12$, $-14 \le l \le 14$	$-13 \le h \le 13$, $-8 \le k \le 14$, $-17 \le l \le 19$	$-12 \le h \le 12$, $-14 \le k \le 14$, $-15 \le l \le 15$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.059	1.074	1.042
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0330$, $wR2 = 0.0919$	$R1 = 0.0351$, $wR2 = 0.0898$	$R1 = 0.0387$, $wR2 = 0.0953$
R indices (all data)	$R1 = 0.0365$, $wR2 = 0.0950$	$R1 = 0.0502$, $wR2 = 0.0993$	$R1 = 0.0505$, $wR2 = 0.1025$
Largest diff. peak and hole ($e\,Å^{-3}$)	0.256 and −0.188	0.321 and −0.140	0.318 and −0.191

Table 3. Norbornene polymerization with complex **1**–**4**/MAO.

Entry	Complex[a]	T (°C)	Yield (g)	Activity (10^{-6})[b]	M_n (10^{-5})	M_w/M_n
1	**1**	25	0.61	0.398	7.69	1.47
2	**1**	40	0.72	0.471	11.3	1.52
3	**1**	60	1.14	0.746	4.75	1.87
4	**1**	80	2.07	1.354	3.14	1.97
5	**2**	20	0.04	0.022	9.36	1.31
6	**2**	40	0.29	0.157	7.53	1.49
7	**2**	60	0.46	0.249	6.83	1.51
8	**2**	80	0.60	0.326	4.17	1.74
9	**3**	30	0.19	0.152	9.21	1.71
10	**3**	40	0.42	0.324	9.95	1.67
11	**3**	60	2.09	1.630	5.49	1.79
12	**3**	80	2.10	1.637	4.31	1.99
13	**4**	30	0.83	0.553	8.11	1.69
14	**4**	40	1.40	0.934	8.26	1.72
15	**4**	60	1.47	0.979	7.87	1.68
16	**4**	80	1.50	1.021	5.85	1.83

[a] 1 mg Ni complex; [MAO]/[Ni] = 1000; reaction volume, 25 mL; polymerization for 1 h.

[b] Activity unit: g polymer (molNi) $^{-1}h^{-1}$.

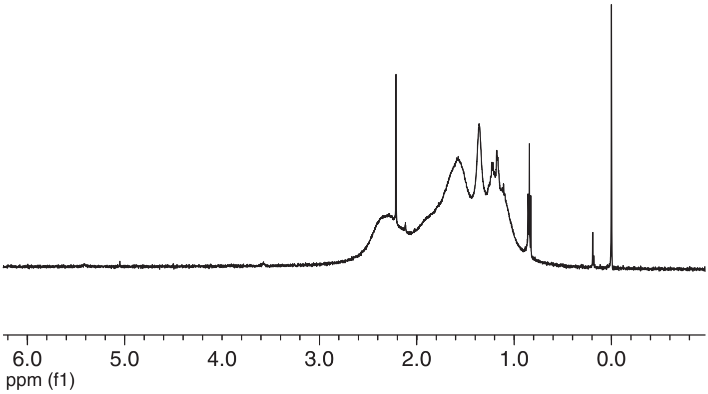


Figure 4. ^{1}H-NMR spectrum of PNBE obtained with complex **1**.

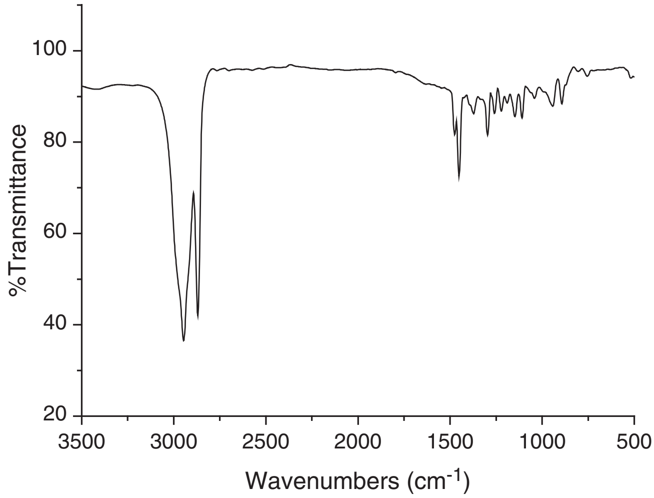


Figure 5. FTIR spectrum of PNBE by complex **1**.

mixture was refluxed with a Dean-Stock apparatus to remove water for 16 h. The resulting solution was evaporated under vacuum to remove the solvent. The remaining residue then was crytallized in hexane, giving 5.41g of light yellow crystals (yield: 72.3%, m.p.: 158°C). Anal. Calcd for $C_{20}H_{29}NO$: C, 80.21; H, 9.76; N, 4.68. Found: C, 80.11; H, 9.86; N, 4.55. ^{1}H NMR ($CDCl_3$): δ (ppm): 12.6 (w, 1H, –NH); 7.1–7.3 (3H, $-C_6H_3(iPr)_2$); 3.0 (2H, 2 $-CH(CH_3)_2$); 2.4 (2H, $-CH_2-$); 2.1 (s, 3H, $CH_3C(O)-$); 1.9 (2H, $-CH_2-$); 1.7(2H, $-CH_2-$); 1.5 (2H, $-CH_2-$); 1.1–1.2 (d, 12H, 2 $-CH(CH_3)_2$).

3.1.2. [2-$CH_3C(O)C_6H_9(=NAr)$] (L2, Ar = 2,6-$Me_2C_6H_3$). The desired product was prepared by reaction of 2-acetylcyclohexanone (3.40 mL, 0.025 mol) and 2,6-dimethylaniline (3.10 mL, 0.025 mol) in the manner analogous to the procedure for **L1**. The resulting product is also a light yellow solid 4.33 g (yield: 71.2%, m.p.: 82°C).

Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found: C, 78.90; H, 8.65; N, 5.64. ^{1}H NMR ($CDCl_3$): δ (ppm): 12.5 (w, 1H, –NH); 7.0–7.2 (3H, $-C_6H_3(Me)_2$); 2.4 (2H, $-CH_2-$); 2.1 (9H, CH_3-); 1.9 (2H, $-CH_2-$); 1.7 (2H, $-CH_2-$); 1.5 (2H, $-CH_2-$).

3.1.3. [2-PhC(O)C_6H_9(=NAr)] (L3, Ar = 2,6-^{i}Pr$_2C_6H_3$). 2-benzoylcyclohexanone (3.10 g, 0.015 mol), 2,6-diisopropylphenylamine (3.00 mL, 0.015 mol) and a catalytic amount of *p*-toluenesulfonic acid were combined in toluene (50 mL), and then the mixture was refluxed with a Dean-Stock apparatus to remove water for 16 h. The resulting solution was evaporated under vacuum to remove toluene. The remaining residue was then crystallized in hexane, giving 4.17 g (yield: 76.9%, m.p.: 115°C) of light yellow crystals. Anal. Calcd for $C_{25}H_{31}NO$: C, 82.98; H, 8.64; N, 3.87. Found: C, 82.86; H, 8.76; N, 3.75. ^{1}H NMR ($CDCl_3$): δ (ppm): 13.0 (w, 1H, –NH); 7.1–7.5 (8H, $-C_6H_3(iPr)_2$, $-C_6H_5$); 3.1 (2H, 2 $-CH(CH_3)_2$); 2.4 (2H, $-CH_2-$); 2.0 (2H, $-CH_2-$); 1.5 (4H, $-CH_2-$); 1.1–1.3 (s, 12H, 2–$CH(CH_3)_2$).

3.1.4. [2-PhC(O)C_6H_9(=NAr)] (L4, Ar = 2,6-Me$_2C_6H_3$). The desired product was prepared by reaction of 2-benzoylcyclohexanone (3.10 g, 0.015 mol) and 2,6-dimethylaniline (1.90 mL, 0.015 mol) in the manner analogous to the procedure for **L3**. The resulting product is also a light yellow solid 3.54 g (yield: 77.3%, m.p.: 99°C). Anal. Calcd for $C_{21}H_{23}NO$: C, 82.51; H, 7.53; N, 4.58. Found: C, 82.41; H, 7.61; N, 4.49. ^{1}H NMR ($CDCl_3$): δ (ppm): 12.8 (w, 1H, –NH); 7.1–7.5 (8H, $-C_6H_3(Me)_2$, $-C_6H_5$); 2.4(2H, $-CH_2-$); 2.2 (6H, CH_3-); 2.0 (2H, $-CH_2-$); 1.5 (4H, $-CH_2-CH_2-$).

3.1.5. [2-CH_3C(O)C_6H_8(=NAr)]$_2$Ni (Complex 1, Ar = 2,6-^{i}Pr$_2C_6H_3$). Ketoimine ligand **L1** (0.90 g, 0.003 mol) in toluene (40 mL) was added to a 100 mL flask equipped with a magnetic stirrer. The solution was cooled to −78°C, and then *n*-BuLi (1.20 mL, 2.8 M) in hexane was added dropwise. The reaction mixture was stirred overnight and warmed to room temperature. Then, (DME)$NiBr_2$ (0.47 g, 0.0015 mol) was added to the resulting yellow solution over a pale yellow precipitate. The new mixture was stirred at 40°C for one day; the mixture became a dark green solution with some gray precipitate. The solvent was evaporated under vacuum, and 60 mL dry CH_2Cl_2 was added. After filtering, the solvent was evaporated under vacuum to about 5–10 mL, and then 60 mL hexane was added to the dark residue and a dark green solid appeared. The solid was washed with hexane (two times) after filtering. Drying in vacuum afforded 0.69 g green product (yield: 70.4%, m.p.: 317°C). Anal. Calcd for $C_{40}H_{56}N_2NiO_2$: C, 73.34; H, 8.56; N, 4.29. Found: C, 73.56; H, 8.84; N, 4.01. ^{1}H NMR ($CDCl_3$): δ (ppm): 6.9–7.3 (6H, $-C_6H_3(iPr)_2$); 3.8 (4H, 2, $-CH(CH_3)_2$); 2.0–2.4 (6H, $CH_3C(O)-$); 1.7 (4H, $-CH_2-$); 1.5 (4H, $-CH_2-$); 1.4 (4H, $-CH_2-$); 1.1–1.2 (24H, $CH(CH_3)^2$); 0.8 (4H, $-CH_2-$).

3.1.6. [2-CH_3C(O)C_6H_8(=NAr)]$_2$Ni (Complex 2, Ar = 2,6-Me$_2C_6H_3$). The desired product was prepared by reaction of ketoimine ligand **L2** (1.30 g, 0.005 mol), *n*-BuLi (1.90 mL, 2.8 M) and (DME)$NiBr_2$ (0.83 g, 0.0025 mol) with a similar procedure as for complex **1**. Light green product (1.03 g, yield: 75.7%, m.p.: 343°C) was obtained. Anal. Calcd for $C_{32}H_{40}N_2NiO_2$: C, 70.73; H, 7.42; N, 5.15. Found: C, 70.80; H, 7.31; N, 4.89. ^{1}H NMR ($CDCl_3$): δ (ppm): 6.8–7.3 (6H, $-C_6H_3(Me)_2$); 2.0–2.6 (18H, 6–CH_3); 0.8–1.9 (16H, 8 $-CH_2-$).

3.1.7. [2-PhC(O)C_6H_8(=NAr)]$_2$Ni (Complex 3, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).

Ketoimine ligand **L3** (1.10 g, 0.003 mol) in toluene (40 mL) was added to a 100 mL flask equipped with a magnetic stirrer. The solution was cooled to −78°C, and *n*-BuLi (1.10 mL, 2.8 M) in hexane was added dropwise. The reaction mixture was stirred overnight and warmed to room temperature. Then, (DME)$NiBr_2$ (0.47 g, 0.0015 mol) was added to the resulting yellow solution over a pale yellow precipitate. The new mixture was stirred at 40°C for one day, the mixture became a dark green solution with some gray precipitate. Then the solvent was evaporated under vacuum and 80 mL dry CH_2Cl_2 was added to the dark residue. After filtering, the CH_2Cl_2 solution was concentrated to about 5–10 mL under vacuum, then 60 mL hexane was added to the black residue, and a dark green solid appeared. The solid was washed with hexane after filtering. Drying in vacuum afforded 0.86 g (yield: 73.5%, m.p.: 294°C) of green product. Anal. Calcd for $C_{50}H_{60}N_2NiO_2$: C, 76.95; H, 7.75; N, 3.59. Found: C, 76.76; H, 7.81; N, 3.48. ^{1}H NMR ($CDCl_3$): δ(ppm): 6.2–7.3 (16H, –C_6H_3(iPr)$_2$, –C_6H_5); 4.0 (4H, 2 –CH(CH_3)$_2$); 2.0 (4H, –CH_2–); 1.7 (4H, –CH_2–); 1.3 (8H, –CH_2–); 1.1–1.3 (24H, –CH(CH_3)$_2$).

3.1.8. [2-PhC(O)C_6H_8(=NAr)]$_2$Ni (Complex 4, Ar = 2,6-Me$_2$C$_6$H$_3$).

The desired product was prepared by the reaction of ketoimine ligand **L4** (1.30 g, 0.004 mol), *n*-BuLi (1.50 mL, 2.8 M) and the (DME)$NiBr_2$ (0.67 g, 0.002 mol) with similar procedure as for complex **3**. Light green solid (0.93 g, yield: 65.5%, m.p.: 236°C) was obtained. Anal. Calcd for $C_{42}H_{44}N_2NiO_2$: C, 75.57; H, 6.64; N, 4.19. Found: C, 75.45; H, 6.76; N, 4.07. ^{1}H NMR ($CDCl_3$): δ (ppm): 6.5–7.3 (16H, –C_6H_3(Me)2, –C_6H_5); 2.4 (12H, –CH_3); 2.1(4H, –CH_2–); 1.6 (4H, –CH_2–); 1.3 (8H, –CH_2–).

3.2. *Crystal structure determination*

The crystals were mounted on a glass fiber using the oil drop scan method. Data obtained with the ω–2θ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved using direct methods, while further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package [37, 38]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. Some carbon atoms on cyclohexyl (C2, C3 in complex **1**, C11, C12 in complex **2** and C9–C12 in complex **3**) of each complex are disordered.

3.3. *Olefin polymerization*

A toluene (5–10 mL) solution of NBE or styrene (0.05 mol) and appropriate MAO solution were introduced sequentially into the 50 mL round-bottom glass flask; then the appropriate amount of Ni(II) complex (Al/Ni = 1000) in 5 mL toluene solution was syringed into the well-stirred solution (total reaction volume is about 25 mL). For ethylene, the same reaction volume and contents were used at atmospheric pressure. The contents were continuously stirred for one hour at polymerization temperature. The polymerizations were stopped by addition of excess 10% HCl–C_2H_5OH. The resulting precipitated PNBE was collected and treated by filtering, washing with C_2H_5OH several times, and drying in vacuum at 60°C/12 h to a constant weight.

Supplementary materials

The X-ray crystallographic data for the structures reported in the article have been deposited in the Cambridge Crystallographic Data Centre, CCDC No.247412 for complex **1**, No. 247413 for complex **2** and No. 250742 for complex **3**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK, Fax: (Int code) +44(1223)336-033 or Email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China and the Science Foundation of Guangdong Province. The authors thank Mr. Feng for single-crystal X-ray technical assistance.

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