Novel nickel(II) and copper(II) complexes with phenoxy-imidazole ligands: Syntheses, crystal structures and norbornene addition polymerization

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Abstract

The novel nickel(II) (**1**) and copper(II) (**2**) complexes bearing 2′-(4′,6′-di-*tert*-butylhydroxy-phenyl)-1,4,5-triphenyl imidazole ligand have been synthesized and characterized. The molecular structure analyses of complexes **1** and **2** indicated that Ni(II) centre in **1** adopts a distorted tetrahedral coordination geometry with a dihedral angle of 85.2° between Ni(1)O(1)N(1) plane and Ni(1)O(1A)N(1A) plane, while the Cu(II) centre in **2** represents a distorted square planar coordination geometry with a *cis*-N_2O_2 arrangement of the donor atoms, the dihedral angle being 32° between Cu(1)O(1)N(1) plane and Cu(1)O(1A)N(1A) plane. After activation with methylaluminoxane (MAO), both Ni(II) and Cu(II) complexes can be used as catalysts for the addition polymerization of norbornene (NB). The polynorbornenes (PNBs) are produced with very high polymerization activity (10^8 g PNB mol^{-1} Ni h^{-1}) for Ni(II) complex and moderate catalytic activity (10^5 g PNB mol^{-1} Cu h^{-1}) for Cu(II) complex, respectively. The high molecular weight polynorbornenes (10^6) are obtained for complexes **1** and **2**. Moreover, the distinct effects of polymerization temperature and Al/M ratio on catalytic activities and molecular weights of polymers are discussed.
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1. Introduction

Olefin polymerization of late transition metal catalysts has attracted considerable attention in academic and industrial fields over the past decade [1]. Extraordinary roles have been played by nickel-based catalysts in oligomerization or polymerization of olefin. Nickel catalysts are best known to oligomerize ethylene, dimerize propylene and higher α-olefins, in which there exists the competition between olefin-insertion and chain-transfer processes [2]. Obviously, this is a function of a number of parameters, containing the nature of the ligands and structure of the precatalysts. A large number of papers and patents published in this field show the intense exploration and commercialization of new polymerization technologies [3].

Polynorbornene (PNB) with different structures and properties can be afforded via three corresponding pathways: ring-opening metathesis polymerization (ROMP), cationic or free-radical polymerization, and addition polymerization (Scheme 1) [4]. The first type of polymers contains double bonds in their backbone, which must be further vulcanized or hydrogenated for commercialization. Low molecular weight polymers are formed through 2,7-linkage in the second type of polymerization products. However, in the addition type polynorbornene, the bicyclic structure remains intact and only the π-bond of the cyclo-olefin is opened. This type of specialty polymers exhibits interesting and unique properties like high chemical resistance, high glass transition temperature, large refractive index, low dielectric constant, and excellent optical

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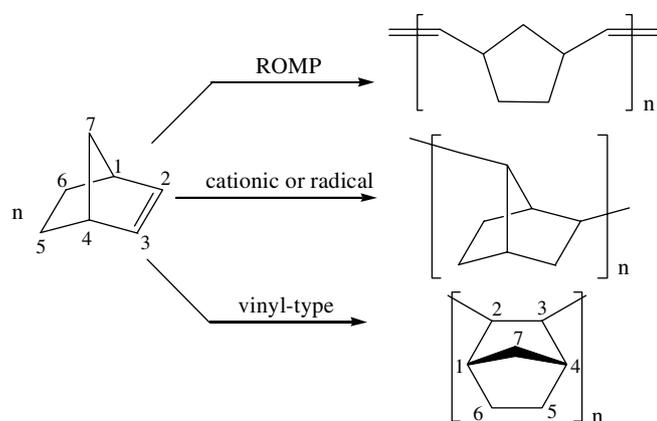
Scheme 1. Schematic representation of the three different types of polymerization for norbornene.

transparency. Driving by industrial application, the addition polymerization of norbornene has inspired the interest of chemists and chemical engineers [5].

In 2001, Janiak and Lassahn [4a] gave an overall review on the vinyl addition polymerization of norbornene using various metal complexes as catalysts, including early transition metals (zirconium and titanium) and late transition metals (palladium and nickel). After Deming and Novak [6] introduced the first nickel complex for the vinyl addition polymerization of norbornene, several other catalyst systems have also been applied to this polymerization reaction [7]. However, copper-based catalysts are considerably rare for olefin polymerization in literatures reported [8], although copper (II) catalysts possess some unique properties in both homo- and copolymerization of olefins with function monomers [9]. In vinyl addition polymerization of norbornene, only a few examples are reported so far [10].

In our research, considerable effort has been devoted to design and synthesize novel olefin polymerization catalysts bearing [N, O], [N, N], and [N, P] ligands. Good catalytic activities have been exhibited by some catalysts in the polymerization of ethylene and norbornene [11]. In recent years, [N, O] bidentate ligand has been one of our preferred objects. Considering the bulky steric hinder and electronic conjugative effect, in this contribution, we prepared a phenol-imidazole [N, O] bidentate ligand, (2′-(4′,6′-di-tert-buty-

lhydroxy-phenyl)-1,4,5-triphenyl imidazole (LH). The novel nickel(II) and copper(II) complexes, bis{(2′-(4′,6′-di-tert-butylhydroxy-phenyl)-1,4,5-triphenyl imidazole)}nickel (NiL₂) (1) and bis{(2′-(4′,6′-di-tert-butylhydroxy-phenyl)-1,4,5-triphenyl imidazole)}copper (CuL₂) (2), have been synthesized and characterized. Preliminary results from the complexes catalyzing norbornene polymerization after activation with methylaluminoxane (MAO) are investigated. The ultrahigh catalytic activity (10^8 g PNB mol^{-1} Ni h^{-1}) is observed for addition polymerization of norbornene in the nickel(II)/MAO system.

2. Results and discussion

2.1. Preparation of ligands and complexes

The syntheses of the nickel and copper complexes as catalytic precursors are shown in Scheme 2. According to a modified method [12], the phenol-imidazole ligand was efficiently synthesized. Complex formation was achieved by treatment of NiCl₂ or CuBr₂ with 2 equiv. of the lithium salt of the phenol-imidazole ligand obtained by the reaction of the ligand with ^{n}BuLi. The attempts to obtain the complexes by direct reaction of Ni(OAc)₂ · 4H₂O or Cu-(OAc)₂ · 2H₂O with the phenol-imidazole ligand are not particularly successful. Crystal suitable for X-ray crystallography of complex 1 or 2 was obtained by slow diffusion of hexane into the dichloromethane solution of complex 1 or 2.

The structures of complexes 1 and 2 are shown in Figs. 1 and 2, respectively. The crystallographic data and refinement parameters of 1 and 2 are summarized in Table 3. For nickel (1) and copper (2) complexes, each ligand acts as an N,O-bidentate ligand and each metal possesses four-coordinate N_2O_2-coordination sphere. The Ni(II) centre of complex 1 represents a distorted tetrahedral coordination geometry with a dihedral angle of 85.2° between Ni(1)O(1)N(1) plane and Ni(1)O(1A)N(1A) plane, while the Cu(II) centre of complex 2 possesses a distorted square planar coordination geometry with a cis-N_2O_2 arrangement of the donor atoms, the dihedral angle being 32° between Cu(1)O(1)N(1) plane and Cu(1)O(1A)N(1A) plane. It is noticeable that the coordinate geometry of the metal Ni(II) obviously deviates from the preferred square planar struc-
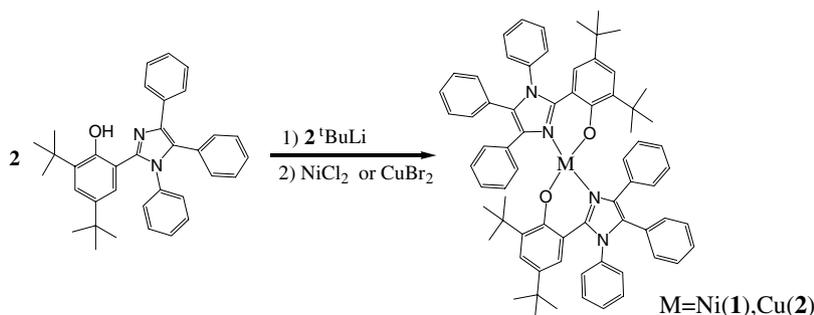
Scheme 2. Synthesis of nickel (1) and copper (2) complexes.
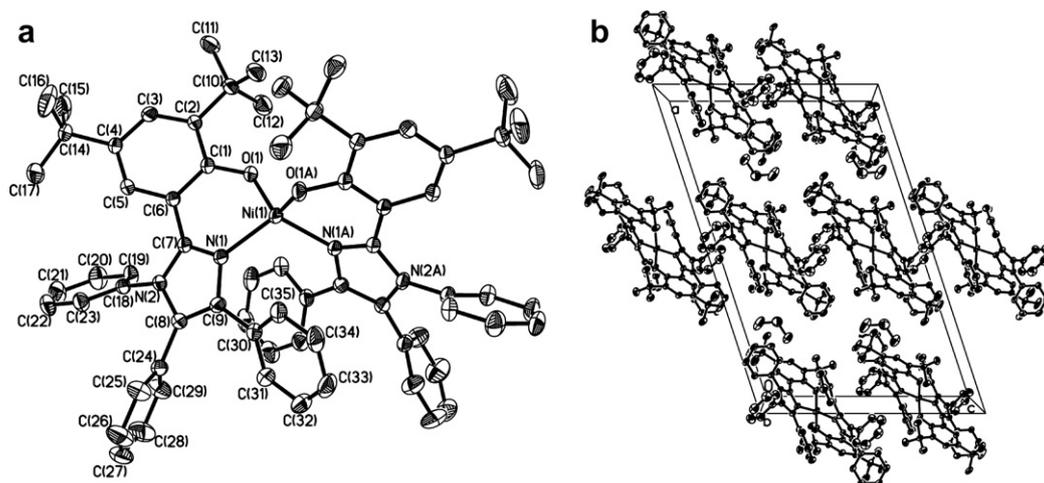
Fig. 1. (a) ORTEP drawing of complex **1**. The hydrogen atoms and solvent molecules are omitted for clarity. (b) Molecular packing diagram of **1**. Selected bond lengths (Å) and angles (°): Ni(1)–O(1) 1.884(3); Ni(1)–N(1) 1.971(2); O(1)–Ni(1)–N(1) 92.64(8); O(1)–Ni(1)–O(1A) 118.18(13); O(1A)–Ni(1)–N(1) 121.31(9); N(1)–Ni(1)–N(1A) 113.17(12).
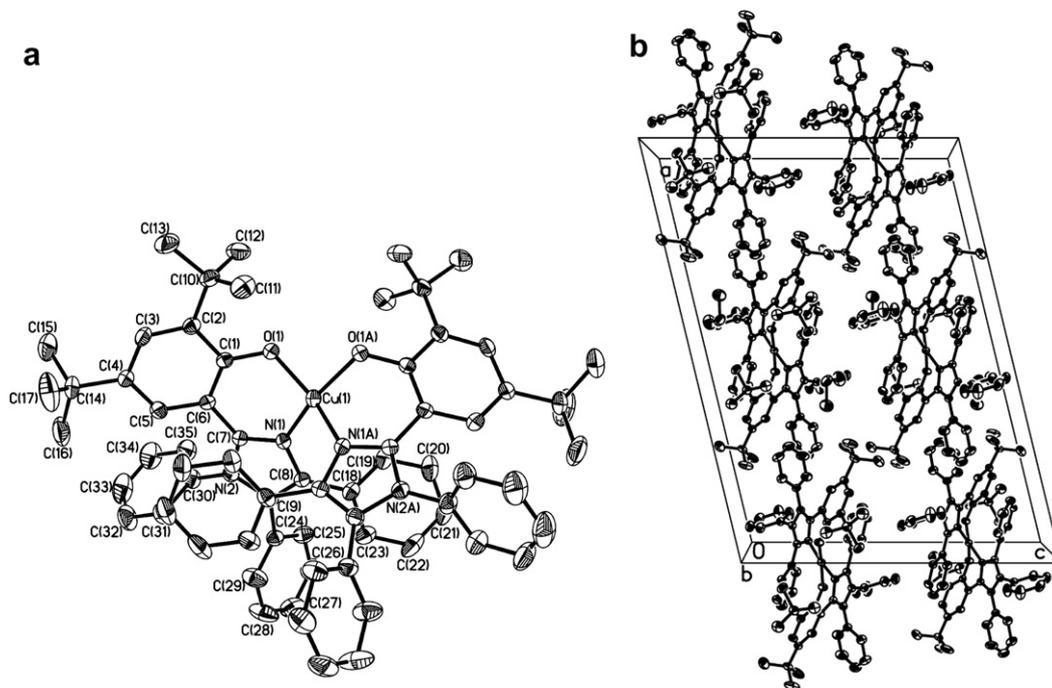
Fig. 2. (a) The molecular structure of complex **2**. (b) Molecular packing diagram of **2**. The hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.891(2); Cu(1)–N(1) 1.945(2); O(1)–Cu(1)–N(1) 88.12(10); O(1A)–Cu(1)–O(1) 93.84(13); O(1)–Cu(1)–N(1A)157.78(9); N(1A)–Cu(1)–N(1) 98.37(15).

ture and takes distorted tetrahedral coordination geometry because of the steric hindrance of the butyl of phenol and a phenyl group of imidazole ring.[13] The Ni(1)–O and Ni(1)–N distances are 1.884(3) and 1.971(2) Å, respectively, which are longer than those (1.828(6) and 1.908(7) Å, respectively) found in the bis[(N-2,6-diisopropylphenyl)salicylaldiminate]nickel(II) complex [14]. The lengths of Cu(1)–O and Cu(1)–N (1.891(2) and 1.945(2) Å, respectively) are similar to those of bis(salicylaldiminate)copper(II) complex [15].

The X-ray analysis shows that there exist two intramolecular π–π interactions between the phenyl ring at 4-position (C9) of imidazole of one ligand and the phenol and/or imidazole ring of the other ligand in the molecular structures of both **1** and **2** (see Fig. 3) [16]. For complex **2**, the weak intermolecular H–π interactions are formed between the hydrogen of a phenyl ring at 1-position (N2) of imidazole in one molecule and a phenol ring in the other molecule. The distance between hydrogen atom and the center of phenol ring is 3.18 Å (Fig. 3). The zigzag stacking
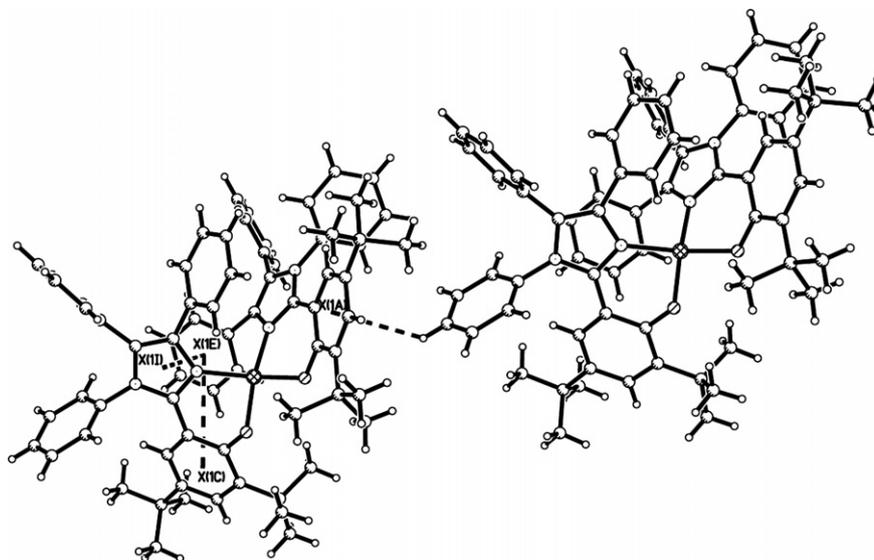
Fig. 3. View of complex **2** showing the intramolecular π–π interactions between the two ligands of the same molecular and intermolecular H–π interactions between hydrogen atom of one molecule and a phenol ring the other molecule.

manner along *c*-axis for **1** and *a*-axis for **2** direction can also be observed (Figs. 1 and 2).

3. Norbornene polymerization

The polymerization results catalyzed by complexes **1** and **2** in the presence of MAO are summarized in Tables 1 and 2. No catalytic activity was observed for complexes **1** and **2** in the absence of MAO. Therefore, the cocatalyst MAO, which can create an empty site for coordination and insertion of the norbornene, is essential for the norbornene polymerization catalyzed by complexes **1** and **2** [17]. After activation with MAO, both Ni(II) and Cu(II) complexes can catalyze norbornene (NB) polymerization.

Variation of the ratio of [Al]/**1** or **2**, which is expressed here as the Al/Ni or Al/Cu ratio, shows a significant effect on the catalytic activities and molecular weight. For Ni(II) complex **1**, the catalytic activities are very high up to

Table 1
Norbornene polymerization for the **1**/MAO catalytic system[a]

Run	Al/Ni	t (°C)	Yield (g)	Activity[b]	M_v^c
1	1000	30	0.902	1.08	1.65
2	2000	30	1.108	1.33	1.82
3	3000	30	1.341	1.61	1.79
4	4000	30	1.525	1.83	2.18
5	5000	30	1.558	1.87	1.77
6	10,000	30	1.908	2.29	1.87
7	4000	15	0.817	0.98	2.32
8	4000	45	1.675	2.01	1.94
9	4000	60	1.117	1.34	1.86
10	4000	75	0.992	1.19	0.98

[a] Polymerization conditions: [Ni] = 0.1 μmol, [NB] = 3.76 g; time = 5 min; V_{total} = 15.0 mL; solvent: chlorobenzene.
[b] 10^8 g PNB mol^{-1} Ni h^{-1}.
[c] 10^6 g mol^{-1}.

Table 2
Norbornene polymerization for the **2**/MAO catalytic system[a]

Run	Al/Cu	t (°C)	Yield (g)	Activity[b]	M_v^c
1	500	60	0.063	12.2	1.83
2	1000	60	0.494	98.7	1.96
3	1500	60	0.578	115.6	2.22
4	2000	60	1.582	316.3	1.92
5	2500	60	0.106	21.1	1.76
6	3000	60	0.018	3.5	1.46
7	2000	30	Trace	–	–
8	2000	45	0.022	4.4	1.79
9	2000	75	0.080	16.0	1.98
10	2000	90	0.058	11.5	2.05

[a] Polymerization conditions: [Cu] = 5 μmol, [NB] = 1.88 g; time = 1 h; V_{total} = 15.0 mL; solvent: chlorobenzene.
[b] 10^3 g PNB mol^{-1} Cu h^{-1}.
[c] 10^6 g mol^{-1}.

10^8 g PNB mol^{-1} Ni h^{-1}. The activities increase with the increase of the Al/Ni ratio under the experimental conditions. When the ratio of Al/Ni was 10,000/1, the highest activity of 2.29×10^8 g PNB mol^{-1} Ni h^{-1} (Table 1, Run 6) is observed. The catalytic polymerization behavior of Cu(II) complex **2** is different from that of Ni(II) complex **1**. The catalytic activities of **2** increases first and then sharply decrease. The highest activity of 3.16×10^5 g PNB mol^{-1} Cu h^{-1} is observed at Al/Cu ratio of 2000/1 (Table 3, Run 4). All polymers display high molecular weights (M_v up to 10^6). The effect of Al/M ratio on molecular weight of polymers is different. For complex **1**, M_v varies irregularly with the increase of Al/Ni ratio, but M_v increases first and then decreases with the increase of Al/Cu ratio for complex **2**.

The large difference of catalytic activities of Ni(II) complex **1** and Cu(II) complex **2** indicates that the nature of the metal center has a significant effect on catalytic activity. Ni(II) complex **1** (up to 2.29×10^8 g PNB mol^{-1} Ni h^{-1},

Table 1, Run 6) is more active than the corresponding Cu(II) complex **2** (up to 3.16×10^5 g PNB mol^{-1} Cu h^{-1}, Table 2, Run 3), which implies that the rate of chain propagation of nickel catalyzed norbornene polymerization is much faster than that of copper catalyzed norbornene polymerization.

The polymerization results catalyzed by complexes **1** and **2** are higher than that of bis[(*N*-2,6-diisopropylphenyl)salicylaldiminate]nickel(II) complex (up to 3.5×10^7 g PNB mol^{-1} Ni h^{-1}) and bis(salicylaldiminate)copper(II) complex (up to 1.5×10^5 g PNB mol^{-1} Cu h^{-1}) [7a,18], especially for Ni(II) complex **1**. The activity of complex **1** is higher with an order of magnitude than that of bis[(*N*-2,6-diisopropylphenyl)salicylaldiminate]nickel(II) complex. The difference results from the difference of molecular structure may be due to the steric hindrance. From Ni(II) complex **1**, the longer Ni(1)–O, Ni(1)–N bond distances (1.884(3) and 1.971(2) Å) make the coordinate atoms (N or O) easier to be removed and form the bare coordinate sites, accordingly benefiting insertion of norbornene.

The reaction temperature also considerably affects the catalytic activities and molecular weight of complexes **1** and **2**. With an increase of reaction temperature, the catalytic activities of complexes **1** and **2** first increase and then decrease. For complex **1**, the maximum value of activities is obtained at 45 °C. For complex **2**, sharp changes can be observed and the highest activity is obtained at 60 °C. For complex **1**, M_v of polymers decreases with increase of reaction temperature, but slight increase for complex **2** with increase of reaction temperature is observed.

The microstructure of the obtained polynorbornene is characterized by ^{1}H NMR and ^{13}C NMR spectra and IR spectra. The polynorbornene have similar ^{1}H NMR and ^{13}C NMR spectra. No resonances are displayed at about δ 5.1 and 5.3 ppm in the ^{1}H NMR spectrum of the polynorbornene, assigned to the *cis* and *trans* form of double bonds [19], which generally indicates the presence of the ring-opening metathesis polymerization (ROMP) structure. The ^{13}C NMR spectrum shows the main four groups of resonances: δ (51.3, 49.4, 48.8, 46.8, 44.5), 38.5, (37.8, 37.4, 34.7), (30.5, 28.7) ppm, attributed to carbons 2 and 3, carbons 1 and 4, carbon 7, carbons 5 and 6, respectively (Scheme 1) [20,21]. The ^{13}C NMR spectrum is similar to that reported by Wu et al. [20] and Patil et al. [7a]. These data indicate that the polynorbornene obtained with the aforementioned catalysts was a vinyl-type (2,3-linked) addition product, i.e. no ROMP was observed. And the ^{13}C NMR spectrum shows that the polymer is *exo* enchained; the spectrum does not exhibit resonances in the δ 20–24 ppm region. The presence of such resonances has been taken as evidence of *endo* enchainment on the basis of mode studies [21]. The multiplicity of the peaks suggests that the insertion of monomer units can take place in more than one stereospecific way, and therefore the obtained polynorbornenes is atactic [22]. Indeed, all polynorbornenes are soluble at room temperature in chlorobenzene and cyclohexane, which indicate low stereoregularity [23].

All polynorbornenes obtained show similar IR spectra. IR spectra reveal the characteristic signals of polynorbornenes at about 943 cm^{-1}. And there are no absorptions at 1680–1620 cm^{-1}, especially about 960 and 735 cm^{-1}, assigned to the *trans* and *cis* forms of double bonds, respectively, which are characteristic of the ROMP structure of polynorbornenes [24]. These absorption peaks at about 943 cm^{-1} can be assigned to the ring system of bicycle[2.2.1]heptane, as Kennedy noted [25].

All the polynorbornenes synthesized here are easily soluble in cyclohexane, chlorobenzene and *o*-dichlorobenzene, which indicate low stereoregularity. Indeed, analysis by wide-angle X-ray diffractometry shows no indication of crystallinity. The attempts to determine the glass transition temperature (T_g) of polynorbornenes failed, since DSC studies did not give an endothermic signal upon heating to 400 °C [11a].

4. Conclusions

The crystal structures show that the four coordination metal centers of nickel(II) metal (**1**) and copper(II) (**2**) complexes with phenoxy-imidazole ligands take the form of distorted tetrahedral and distorted square planar coordination geometries, respectively. Due to the steric effects of adjacent groups, a more crowded steric environment for nickel(II) center makes it obviously deviated from the usual planar *trans*-N$_2$O$_2$ coordination geometry.

Preliminary experiments indicated that complexes **1** and **2** can be used as the precursor for the catalysis of norbornene polymerization in the presence of MAO. To the best of our knowledge, this is one of the catalysts possessing highest activities for vinyl addition polymerization of norbornene in reported literatures either to nickel complex or to copper complex.

5. Experimental

5.1. General procedures

All air-sensitive experiments were carried out under nitrogen using standard Schlenk and vacuum-line techniques. Chlorobenzene was dried over CaH$_2$ and distilled under nitrogen prior to use. Norbornene was purchased from ACROS and purified by distillation over sodium. Methylaluminoxane (MAO) was purchased from Aldrich as 10% weight of a toluene solution and used without further purification. Other chemicals were of analytical grade and were used as received. IR spectra were recorded on a Niclolet FT-IR spectrometer. Element analyses were performed on an Elementar vario EL III Analyzer. ^{1}H NMR and ^{13}C NMR spectra were carried out on a Bruker AC 500 spectrometer instrument at room temperature in CDCl$_3$ solution for ligands and complexes, and *o*-dichlorobenzene-d$_4$ solution for polymers using TMS as an internal standard. The intrinsic viscosity [η] was measured in chlorobenzene at 25 °C using an Ubbelohde viscometer. Viscosity average

molecular weight (M_v) values of polymer were calculated by the following equation: $[\eta] = 5.97 \times 10^{-4} M_v^{0.56}$ [26,27]. Differential scanning calorimetric (DSC) measurements were performed on a Perkin–Elmer Pyris 1 DSC. The wide-angle X-ray diffraction (WAXD) diagram of the polymer powders was obtained using a Bruker D4 Endeavor X-ray diffractometer with monochromatic radiation at a wavelength of 1.54 Å. Scanning was performed with 2θ ranging from 5° to 60°.

5.2. Synthesis of ligand [2'-(4',6'-di-tert-butylhydroxyphenyl)-1,4,5-triphenyl imidazole] (LH)

Analogous to the literature reported previously [12], a 25 mmol of benzyl and 25 mmol of 3,5-di-tert-butylhydroxybenzaldehyde were dissolved in 100 mL glacial acetic acid at room temperature. Aniline (37.5 mmol) was added dropwise to this solution, and 125 mmol ammonium acetate was added subsequently. The mixture was heated at 110 °C for 12 h. After the termination of the reaction, the yellow solution was poured into a copious amount of water. Recrystallization from an ethyl acetate solution afforded 7.35 g of white powder with a 59% overall yield. ^{1}H NMR (500 MHz, CDCl$_3$, ppm) δ 0.90(s, 9H, tBu), 1.49(s, 9H, tBu), 6.61(d, 1H, Ar$_{OH}$H), 7.19(d, Ar$_{OH}$H), 7.20–7.25(m, 11H, ArH), 7.34(d, 3H, ArH), 7.55(d, 1H, ArH), 13.4-(1H, OH). IR (kBr, cm^{-1}): $\bar{v}$ 3419(br), 3061(w), 2957(s), 2906(m), 2867(m), 2641(w), 1560(m), 1485(s), 1441(s), 1395(s), 1360(m), 1251(s), 1278(m), 1227(m), 1187-(w), 1076(w), 1025(w), 876(w), 849(m), 768(m), 697(s), 668(w). Elemental Anal. Calc. for C$_{35}$H$_{36}$N$_2$O: C, 83.96; H, 7.25; N, 5.60. Found: C, 83.89; H, 7.21; N, 5.60%.

5.3. Synthesis of nickel complexes (NiL$_2$) (1)

To a solution of ligand (LH) (4 mmol, 1.868 g) in 20 mL of THF was added dropwise a 1.6 M solution of ^{n}BuLi in hexane (4 mmol, 2.5 mL). A light yellow solution was obtained. After 2 h of reaction, the resulting lithium salt solution was added dropwise to the suspension of anhydrous NiCl$_2$ (2 mmol, 0.259 g) in 20 mL CH$_2$Cl$_2$; a dark red solution was formed, then stirred for 6 h at room temperature. The solution obtained was dried in vacuo, and the residue was extracted with 30 mL of dichloromethane and recrystallized from a dichloromethane/hexane solution at room temperature to give complex 1 as yellow crystals in 46% yield. IR (KBr, cm^{-1}): $\bar{v}$ 3059(w), 2950(s), 2904(m), 2866(m), 2364(w), 1600(m), 1497(s), 1458(m), 1384(m), 1310(m), 1262(s), 1075(w), 919(w), 794(w), 768(m), 699(s). Elemental Anal. Calc. for C$_{70}$H$_{70}$NiN$_4$O$_2$2CH$_2$Cl$_2$: C, 70.43; H, 6.07; N, 4.56. Found: C, 70.79; H, 6.28; N, 4.51%.

5.4. Synthesis of copper complexes (CuL$_2$) (2)

Analogous synthesis to 1, except that anhydrous CuBr$_2$ instead of anhydrous NiCl$_2$. Green crystals in 61% yield. IR (KBr, cm^{-1}): $\bar{v}$ 3063(w), 2959(s), 2899(m), 2863(m),

2356(w), 2340(w), 1580(m), 1496(s), 1429(s), 1384(m), 1299(m), 1260(s), 1018(m), 796(m), 779(m), 762(m), 729(s), 698(s). Elemental Anal. Calc. for C$_{70}$H$_{70}$CuN$_4$O$_2$ · 2CH$_2$Cl$_2$: C, 70.15; H, 6.05; N, 4.54. Found: C, 70.16; H, 6.13; N, 4.46%.

5.5. X-ray crystallography

Diffraction data of complexes 1 and 2 were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All the data were collected at room temperature and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL) [28], absorption corrections were applied to the data. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. A summary of the crystallographic data and selected experimental information is given in Table 3.

5.6. Polymerization of norbornene

In a typical procedure (Table 1, Run 5), 0.1 μmol of nickel complex 1 in 2.0 mL of chlorobenzene, 3.76 g of norbornene in 8.0 mL of chlorobenzene and 5.0 mL of fresh chlorobenzene were added into a special polymerization bottle (25 mL) with a strong stirrer under nitrogen atmosphere. After the mixture was kept at 30 °C for 10 min, 0.33 mL of MAO was charged into the polymerization system via a syringe and the reaction was started. Five minutes later, acidic ethanol ($V_{ethanol}$:$V_{concd.HCl} = 20:1$) was

Table 3
Crystal data and structure refinement for complexes 1 and 2

Complex	1	2
Formula	C$_{72}$H$_{74}$Cl$_4$N$_4$NiO$_2$	C$_{72}$H$_{74}$Cl$_4$CuN$_4$O$_2$
F_w	1227.86	1232.69
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a (Å)	28.473(10)	27.231(7)
b (Å)	13.024(5)	12.303(3)
c (Å)	18.500(7)	19.897(5)
α (°)	90	90
β (°)	108.064(5)	103.575(4)
γ (°)	90	90
V (Å^3)	6522(4)	6480(3)
Z	4	4
ρ_{calcd} (Mg m^{-3})	1.250	1.264
μ (mm^{-1})	0.509	0.550
$F(000)$	2584	2588
Reflections collected	16,004	16,003
Independent reflections	7157	7085
R(int)	0.0588	0.0784
Data/restraints/parameters	7157/0/381	7085/0/381
GOF on F^2	0.939	0.773
R_1, wR_2 [$I > 2\sigma(I)$] [a]	0.0596, 0.1525	0.0580, 0.1089
Largest difference in peak and hole (e Å^{-3})	0.546 and −0.473	1.069 and −0.376

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$, $wR_2 = [\sum(|F_o|^2 - |F_c|^2)^2/\sum(F_o^2)]^{1/2}$.

added to terminate the reaction. The PNB was isolated by filtration, washed with ethanol and dried at 80 °C for 48 h under vacuum. For all polymerization procedures, the total reaction volume was 15.0 mL, which can be achieved by the variation of the amount of chlorobenzene when necessary. IR (KBr): 2944, 2871, 1474, 1451, 1377, 1296, 1260, 1220, 1141, 1102, 1020, 940, 902, 864, 800 cm^{-1}. ^{1}H NMR: δ 0.7–3.0 (m, maxima at 1.29 1.71 2.05 2.36 ppm).

Acknowledgements

Appendix A. Supplementary material

CCDC 636922 and 636923 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.04.010.

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