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Vinyl addition polymerization of norbornene catalyzed by β-iminoamine Ni(II) complexes/methylaluminoxane systems

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Two nickel(II) complexes (**A** and **B**) bearing β-iminoamine ligands, [2-(ArN=CH)-C_6H_4-NMe_2] (**La**, Ar = 2,6-i-$Pr_2C_6H_3$; **Lb**, Ar = 2,6-$Me_2C_6H_3$), were synthesized and characterized by elemental analyses and ^{1}H NMR. X-ray crystal structure of complex **B** reveals that the six-membered chelate ring adopts a envelope conformation, with nickel(II) atom deviating from the plane of backbone aromatic ring by 1.164 Å. In the presence of methylaluminoxane (MAO), both complexes showed moderate activities of 10^5 g mol_{Ni}^{-1} h^{-1} for norbornene polymerization. β-iminoamine Ni(II)/MAO catalysts gave unimodal polymers (M_w, 3.16–8.02 × 10^5 g/mol) with a relatively narrow MWD (M_w/M_n, 1.59–2.14), indicative of single-site catalyst behavior. The obtained polymers are vinyl-type polynorbornenes (PNBs), which are soluble in common solvents such as toluene, cyclohexane and dichlorobenzene.

1. Introduction

Norbornenes represent a wide range of monomers derived from dicyclopentadiene (DCPD) by Diels–Alder reaction. Norbornenes can be polymerized via ring opening metathesis polymerization (ROMP), cationic or radical polymerization and vinyl addition polymerization [1–3]. Through the choice of catalyst, each route leads to its own polymers with different chain structure (Fig. 1) [2]. The vinyl-type polynorbornenes (PNBs) obtained with early transition metal catalysts are usually crystalline and insoluble polymers [4], which are brittle and unsuitable for applications. In the 1990s, cycloolefin copolymers (COCs) had been successfully prepared by using metallocene catalysts [5–7]. These saturated copolymers have excellent properties such as high transparency, high temperature capability and good processability. In early 1990s, Risse and coworkers [8–10] reported that norbornene could be polymerized to soluble amorphous polymers, by using a series of late transition metal (LTM) catalysts ([Pd(RCN)$_4$][BF$_4$]$_2$). Since then, the research interests of vinylic polymerization of norbornene were turned to LTM catalysts [1]. In 1995, the discoveries of Ni(II)- and Pd(II)-α-diimine catalysts by Brookhart [11] have aroused general interest in LTM catalyst systems [12–14] (Fig. 2).

It was generally accepted that the catalyst nature (cationic or neutral), the size of steric hindrance and the size of chelate ring play important roles in ethylene polymerization [15]. The cationic Ni(II)- and Pd(II)-based α-diimine catalysts are very active for ethylene polymerization [11,16]. In contrast, they were reported to be inactive or less active catalysts for norbornene homopolymerization [17–19]. The neutral anilinotropone-based Ni(II) systems are relatively less active in ethylene polymerization than the cationic Ni(II)-α-diimine systems [20,21]. Comparing with the cationic Ni(II)-α-diimine systems, cationic Ni(II)-β-diimine systems are much less active in ethylene polymerization [22,23]. However, these cationic six-membered ring systems were found to be considerably active in norbornene homopolymerization [24]. The neutral Ni(II)-β-diketiminato systems are moderately active catalysts for both norbornene polymerization and ethylene polymerization [23,24]. The neutral Ni(II)-salicylaldimine systems were reported to be very active catalysts for norbornene polymerization [25–27]. The neutral Ni(II)-salicylaldimine systems bearing bulky R′ substituent (Fig. 2) also exhibited high activity for ethylene polymerization [28,29]. That said there is still a lack of understanding on the nature of the active species to understand the activity trends [2].

The discussed β-iminoamine Ni(II) complexes are six-membered chelates with steric hindrance on one side (Fig. 2).

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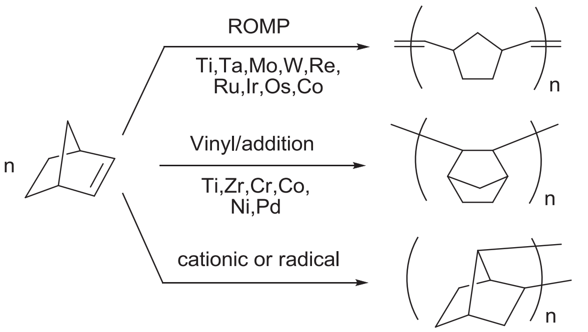


Fig. 1. The three different types of norbornene polymerization through the choice of catalyst [2].

Upon activation with MAO, these Ni(II) precursors would generate cationic Ni(II) active species [11,30], which should possess a sterically open nature. In this paper, norbornene polymerization behavior of these six-membered chelates was reported. Influences of temperature, Al/Ni ratios and precursor structure on polymerization behavior were examined.

2. Results and discussion

2.1. Synthesis of ligands (**La** and **Lb**) and nickel(II) complexes (**A** and **B**)

The synthetic routes of ligands and complexes were shown in Scheme 1. 2-(Dimethylamino)benzaldehyde was prepared in a one-pot procedure [31]. The ratio of *n*-butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (TMEDA) should be less than 1:1 in the *o*-metallization step [32]. The condensations of 2-(dimethylamino)benzaldehyde with the aromatic amines were carried out in toluene at 80 °C, with formic acid as catalyst. The coordination of ligands to nickel(II) ions was preformed in dichloromethane (DCM) at room temperature. Filtration of the reaction mixture gave clear dark-purple filtrate. Crystals of complexes were obtained by precipitating the concentrated filtrate with *n*-hexane. Both complexes are slightly sensitive to moisture and soluble in chloroform. Complex **A** is more soluble in toluene than complex **B**. Exposure of these blue-purple crystals to vacuum or to dry nitrogen resulted in opaque purple compounds, due to lose of solvent from the crystals. Thus, it should be noted that, for both complexes, elemental analysis gave results that are consistently low, which are close to the calculated values of the unsolvated complexes because the lose of the solvated dichloromethane in storage and in operation. Single crystals suitable for X-ray diffraction studies were obtained by layering a DCM solution of complex **B** with *n*-hexane, as a mono-dichloromethane solvate.

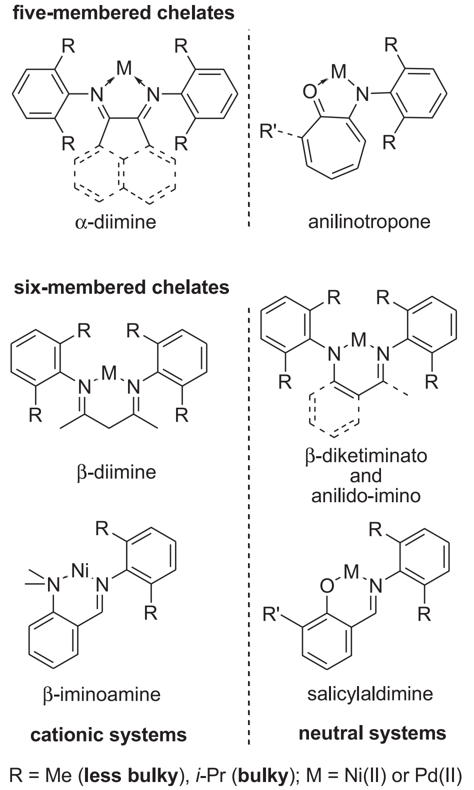
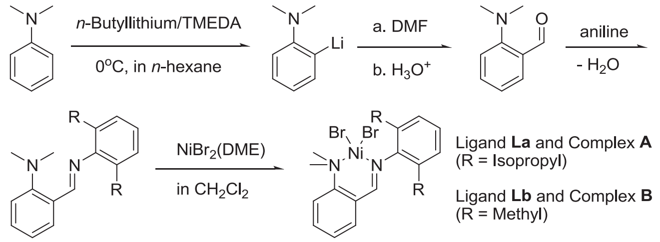


Fig. 2. Ligand series of related catalyst precursors (auxiliary ligands on metal were omitted).



Scheme 1. Synthesis of β-amino-imine ligands and corresponding Ni(II) complexes.

2.2. Crystal structure of nickel complex **B**

The ORTEP diagrams of complex **B**, the selected bond distances and angles are shown in Fig. 3. The ratio of complex molecules with mutual mirror conformation is 1:1 in a packing diagram. The

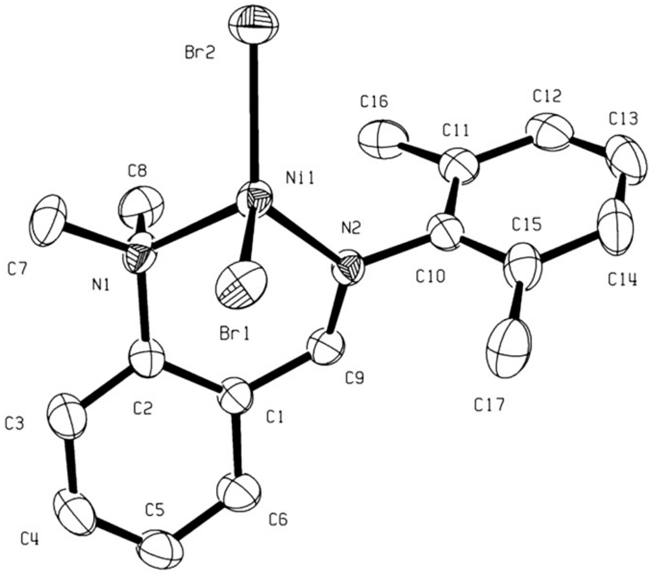


Fig. 3. ORTEP view of complex **B** is drawn with thermal ellipsoids at the 30% probability level. Hydrogen atoms and the cocrystallized methylene dichloride molecule are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni–Br1 2.3507(9), Ni–Br2 2.3524(8), Ni–N1 2.028(4), Ni–N2 1.974(4), N1–C2 1.472(6), N1–C7 1.489(6), N1–C8 1.489(7), N2–C9 1.280(6), N2–C10 1.455(6), C1–C9 1.450(6), C1–C2 1.398(6); N1–Ni–N2 92.27(15), Br1–Ni–Br2 120.26(3), N1–Ni–Br1 103.42(12), N1–Ni–Br2 109.34(12), N2–Ni–Br1 110.03(11), N2–Ni–Br2 116.85(11), C2–N1–Ni 111.5(3), C9–N2–Ni 120.8(3), C1–C2–N1 118.6(4), C1–C9–N2 126.0(4), C2–C1–C9 126.6(4).

crystal structure of complex **B** reveals that Ni(II) atom is coordinated in a tetrahedral geometry. The N1–Ni–N2 bite angle in complex **B** is 92.27(15)°, which is smaller than that observed in β-diimine Ni(II) complex (93.7(2)°) [22] and larger than that observed in α-diimine Ni(II) complex (82.6(2)°) [33]. The six-membered chelate ring adopts an envelope conformation with a C2–C1–C9–N2 torsion angle of 18.05°, which is larger than that found in anilido-imino nickel complexes (10.42°) [34]. The distance from Ni(II) atom to the plane of backbone aromatic ring is 1.164 Å, which is larger than that observed in anilido-imino nickel complexes (0.366 Å) [34].

2.3. ^{1}H NMR spectra of paramagnetic complexes *A* and *B*

^{1}H NMR spectra of paramagnetic complexes in $CDCl_3$ are shown in Fig. 4. Most of the resonance peaks can be assigned to appropriate protons as marked in Fig. 4. A clean spectrum of complex **B** made it possible to discriminate the signal of **a** (1.77 ppm) from the signal of impurities (from free ligand, *), by comparing their integral values with that of the other peaks. In the spectrum of complex **A**, the signal of **a** (1.68 ppm) was overlapped by the signals of impurities (from *n*-hexane, 0.88, 1.29–1.31 ppm). The **i**&**i**′ signal of complex **A** was considered to be the broaden peak centered at 7.66 ppm. In a static structure (Fig. 3), the methyl groups should give a different chemical shift because they would be in a different orientation in space. It might be reasonable to ascribed the coincidence of the methyl signals, **e**&**e**′ and **i**&**i**′, to the "boat-to-boat" conversion of the six-membered chelate ring [35]. The observed chemical shift (δ_{obs}) in paramagnetic compounds can be divided into three parts, the diamagnetic shifts (δ_{dia}), the Fermi contact (δ_{con}) and the dipolar contribution (δ_{dip}, which can be very small compared with δ_{con}) [36,37]. The contribution of δ_{dia} and δ_{con} to δ_{obs} should be equal to the protons in the paired methyl groups. The dipolar contribution (δ_{dip}) is strongly dependent on the distance between the paramagnetic center and the nucleus and the orientation in space, and the contribution of the later is often small in orthorhombic system [37]. The splitting singals of ^{i}Pr groups, of which the two methyl groups would stay above and below the aniline plane, respectively [38], suggest that the Ni–H distance would play a more important role than the orientation in space (Fig. 3). The ranges of the Ni–H distance, measured in crystal of complex **B**, are 2.812–3.754 Å for N-methyl groups and 3.287–4.805 Å for Ar-methyl groups, respectively. Thus, the rotation of methyl groups would also lead to a broad signal. That said, the existence of the paramagnetic core made it difficult to distinguish the chelate-ring conversion from the overlap of signals. Moreover, the chelate-ring conversion, in low or high frequency, should be a quick procedure. The chelate ring in solution would like to adopt a time-averaged conformation, which should be similar to those in crystal.

2.4. Norbornene polymerization

In the presence of MAO, norbornene polymerization experiments were carried out in toluene by using complexes **A** and **B** as catalyst precursors (Table 1). At a constant temperature of 65 °C, the catalyst activities were observed to increase continuously with increasing Al/Ni ratios (entries 1–4, 10, 14, 15; 17, 20, 21). For the selected conditions, the significant increases in activities were, respectively, observed at Al/Ni ratio of 800 for a precatalyst loading of 4 umol (entry 4) and at Al/Ni ratio of 400 for a precatalyst loading of 10 ummol (entry 6). Low Al/Ni ratio would decrease the molecular weight (M_w) and broaden the molecular weight distribution (MWD) (entry 4 vs. 10, entry 6 vs. 8). Excess MAO would gives rise to easy chain transfer because of the influence of $AlMe_3$ [24,39,40], which decreases the molecular weight and give a slightly broaden MWD (entry 15). Higher conversion rates of norbornene can be achieved by adding more catalyst precursors (entry 5–8) as well as by extending the reaction time (entry 13).

The influence of temperatures on polymerization was carried out at a constant Al/Ni ratio of 1000 (entries 9–12, 16–19). The

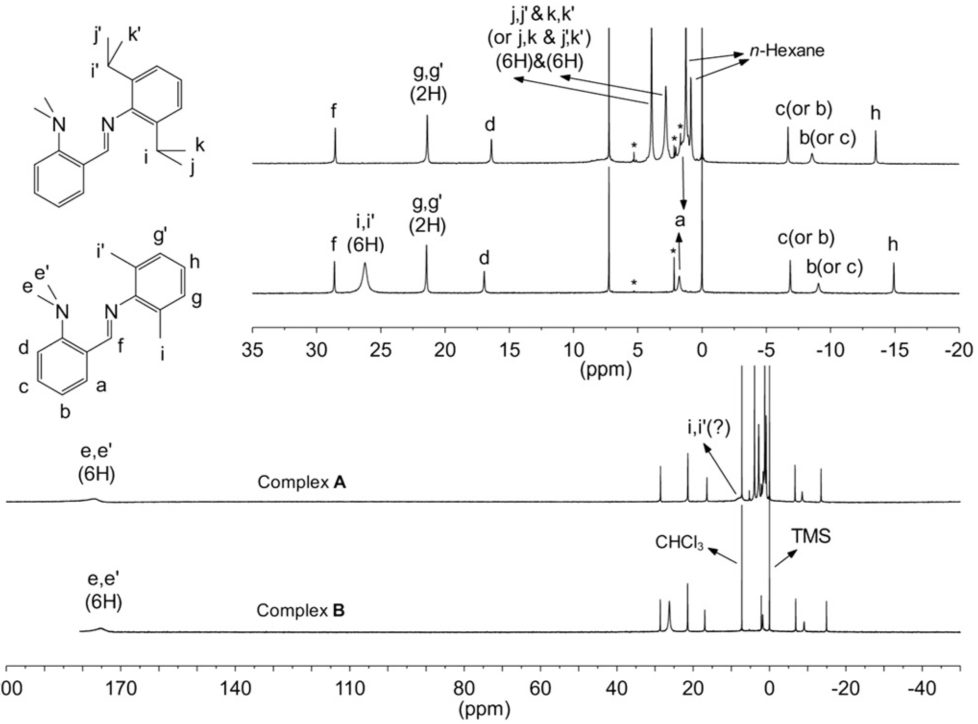


Fig. 4. ^{1}H NMR spectra of Ni(II) complexes **A** and **B** in $CDCl_3$ at 25 °C. Ni and Br atoms were omitted for clarity of labeling. "*" Free ligand impurities.

Table 1
Influence of temperatures and Al/Ni ratios on norbornene polymerizations[a].

Entry	Cat.	μmol	Al/Ni	T_p (°C)	Yield (%)	Activity[b]	M_w [c]	M_w/M_n[c]
1	**A**	4	200	65	3.7	0.69		
2	**A**	4	400	65	5.9	1.11		
3	**A**	4	600	65	12.4	2.34		
4	**A**	4	800	65	21.3	4.01	4.48	1.90
5	**A**	10	200	65	8.2	0.62		
6	**A**	10	400	65	53.7	4.04	3.16	2.14
7	**A**	10	600	65	57.7	4.34		
8	**A**	10	800	65	59.5	4.48	4.79	1.67
9	**A**	4	1000	55	17.8	3.35	8.02	1.68
10	**A**	4	1000	65	24.9	4.68	6.55	1.64
11	**A**	4	1000	75	22.1	4.16	4.34	1.64
12	**A**	4	1000	85	20.0	3.77	3.56	1.61
13	**A**	4	1000	65	32.3	1.01	6.56	1.88
14	**A**	4	1500	65	26.0	4.89		
15	**A**	4	2000	65	29.3	5.51	5.45	1.70
16	**B**	4	1000	55	13.3	2.51	7.13	1.65
17	**B**	4	1000	65	18.0	3.38	5.37	1.71
18	**B**	4	1000	75	20.7	3.90	4.36	1.59
19	**B**	4	1000	85	17.1	3.22	3.54	1.65
20	**B**	4	1500	75	23.7	4.46		
21	**B**	4	2000	75	28.8	5.42		

[a] Polymerization conditions: solvent, toluene; total volume, 20 ml; norbornene, 0.04 mol(3.77 g); reaction time, 30 min (except entry 13, 3 h).

[b] In units of 10^{-5} g PNB/(mol$_{\text{Ni}}$h).

[c] M_w (in units of 10^{-5} g/mol) and M_w/M_n were determined by GPC with standard polystyrene as the reference and with 1,2,4-trichlorobenzene (TCB) as the eluent at 150 °C.

Table 2
Crystal data and structure refinement for complex **B**.

Empirical formula	$C_{18}H_{22}Br_2Cl_2N_2Ni$
Formula weight	555.81
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal size (mm^3)	0.3 × 0.23 × 0.17
Crystal system	Orthorhombic
Space group	Pbca
a (Å)	12.6137(10)
b (Å)	14.4154(12)
c (Å)	24.364(2)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	4430.1(6)
Z	8
Calculated density (Mg/m^3)	1.667
Absorption coefficient (mm^{-1})	4.729
F(000)	2208
θ range for data collection (°)	2.30–25.50
Limiting indices	$-15 \leq h \leq 14$ $-17 \leq k \leq 16$ $-29 \leq l \leq 29$
Reflections collected/unique	24,520/4122 [R(int) = 0.0512]
Completeness to $\theta = 25.50$	100.0%
Absorption correction	None
Max. and min. transmission	0.5003 and 0.3130
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4122/0/230
Goodness-of-fit on F^2	1.051
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0412$, w$R_2 = 0.0995$
R indices (all data)	$R_1 = 0.0794$, w$R_2 = 0.1181$
Largest diff. peak and hole (e Å^{-3})	0.754 and −0.633

catalyst activities increased firstly then decreased gradually with increasing temperature. The result should be ascribed to the opposing effects of the increased temperature on the polymerization rate and catalyst decomposition [41]. At the same temperature, the bulky **A**/MAO catalyst presented slightly higher activities than the less bulky **B**/MAO catalyst. This activity sequence agrees with that observed in β-diimine Ni(II)/MAO and β-diketiminato Ni(II)/MAO systems [24]. Upon increased temperature, molecular weight (M_w) of polymer products decreased with a minor change of MWD (1.59–1.71). The obtained GPC curves of the polymers were all unimodal with narrow molecular weight distributions (1.59–2.14) (Table 1), indicative of single-site catalyst behavior. Compared with the other six-member chelated Ni(II) systems [24–29], the low activity of β-iminoamine Ni(II)/MAO systems should be aroused by the nature of their cationic active species, which possessed a less planar chelate ring.

^{1}H NMR spectra of norbornene polymers, obtained with **A**/MAO at 65 °C and 85 °C (Table 1, entries 10 and 12), are shown in Fig. 5. The absence of proton resonances at 5.15(*cis*) and 5.31(*trans*) ppm, which are related to ROMP polymers, suggests a vinyl addition polymerization pathway of norbornene [17,42]. An unknown peak is present at 5.42 ppm, which is close to the chemical shift of vinyl proton observed in 2-methylnorbornene (5.47 ppm) [43]. It is reasonable to think that the Ni–C bonds of the propagating active species have tendency to be cleaved. However, the intensity of this signal does not increase with increasing temperature. Therefore, the presence of vinyl-type chain end in polymer products needs further confirmation. The obtained norbornene polymers are soluble in common solvents such as toluene, xylene, cyclohexane and chlorobenzene.

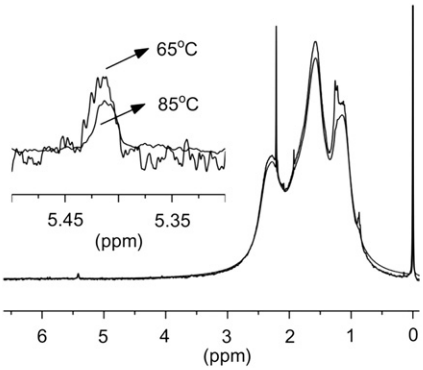


Fig. 5. ^{1}H NMR spectra of norbornene polymers obtained with **A**/MAO at 65 °C and 85 °C (Table 1, entry 10, 12), in 1,2-dichlorobenzene-d4 at 50 °C.

3. Conclusion

β-iminoamine ligands and corresponding Ni(II) complexes were synthesized and characterized. X-ray crystal structure of complex **B** displays that the six-membered chelate ring adopts a envelope conformation, with nickel(II) atom deviating from the plane of backbone aromatic ring by 1.164 Å. In the presence of MAO, β-iminoamine Ni(II) complexes were used as catalyst precursors for norbornene polymerization. The results showed the β-iminoamine Ni(II)/MAO catalysts exhibited an activity level of 10^5 mol$_{\text{Ni}}^{-1}$ h^{-1} and gave vinyl-type polynorbornenes with unimodal and narrow molecular weight distribution (1.59–2.14), indicative of single-site catalyst behavior. The low activity of β-iminoamine Ni(II)/MAO systems should be aroused by the nature of their cationic active species, which possessed a less planar chelate ring.

4. Experimental

4.1. General remarks

All necessary manipulations involving air- and moisture-sensitive compounds were performed by standard Schlenk techniques under nitrogen atmosphere in vacuum-line. 2,6-Diisopropylaniline, 2,6-dimethylaniline and *n*-butyllithium were purchased from Aldrich. *N,N*-dimethylformamide (DMF) was dried on ahydrous $MgSO_4$ and distilled before use. (DME)$NiBr_2$ was prepared according to literature procedures [44]. 2-(Dimethylamino)benzaldehyde, golden yellow liquid (bp: 120–122 °C ~ 12 mmHg), was prepared according to the reported literature [31]. MAO solid was prepared by the controlled hydrolyzation of TMA in toluene at 0–60 °C with grinding $Al_2(SO_4)_3\cdot\cdot 18H_2O$ powders as water source ($H_2O/Al = 1.3$). Hexane and toluene were thoroughly dried over phosphorus pentoxide and sodium, respectively. Norbornene was purchased from Acros, purified by drying over sodium and distillation, used as toluene solution (4.0 mol/L). Other commercially available reagents were purchased and used as received.

^1H NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer. Elemental Analysis was determined with Thermo Scientific Flash 2000 Organic Elemental Analyzer. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution (MWD) of the polymers were performed on a PL-GPC 220 instrument with standard polystyrene as the reference and with 1,2,4-trichlorobenzene (TCB) as the eluent at 150 °C.

4.2. Synthesis of ligands and complexes

4.2.1. 2-(((2,6-Diisopropylphenyl)imino)methyl)-N,N-dimethylaniline (*La*)

La was synthesized by the direct condensation of 2-(dimethylamino)benzaldehyde (0.9 g, 6 mmol) with 2,6-diisopropylaniline (1.1 g, 6 mmol) in 50 ml toluene at 80 °C, with formic acid as catalyst. After hours of heating, the reaction mixture was allowed to cool to room temperature and dried by ahydrous $MgSO_4$. After filtration, toluene was distilled off under vacuum. The remaining yellow oil was chromatographed on a column of neutral alumina or silica gel with *n*-hexane as eluent. Ligand **La** was finally obtained as light yellow crystals after concentration of the eluent and recrystallization from *n*-hexane (yield: 1.2 g, 65%). m.p.: 65–66 °C; Found: C, 81.73; H, 9.18; N, 9.05. Anal. Calc.: C, 81.77; H, 9.15; N, 9.08; ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.17 (d, $J = 7.9$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 1H), 7.10 (ddd, $J = 26.5$, 12.9, 6.8 Hz, 5H), 3.23–2.95 (m, 2H), 2.77 (s, 6H), 1.18 (d, $J = 6.9$ Hz, 12H).

4.2.2. 2-(((2,6-Dimethylphenyl)imino)methyl)-N,N-dimethylaniline (*Lb*)

By using the similar procedure described for ligand **La**, ligand **Lb** was obtained as yellow crystals in 72% yield. m.p.: 93–94 °C; Found: C, 80.85; H, 8.03; N, 11.06. Anal. Calc.: C, 80.91; H, 7.99; N, 11.10; ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.16 (d, $J = 7.1$ Hz, 1H), 7.43 (t, $J = 7.0$ Hz, 1H), 7.11 (dd, $J = 19.6$, 11.5 Hz, 3H), 6.97 (dd, $J = 29.6$, 22.3 Hz, 2H), 2.78 (s, 6H), 2.15 (s, 6H).

4.2.3. ((2,6-diisopropyl)Phenyl-N=CH-C_6H_4-o-N(Me)$_2$)$NiBr_2$ (*A*)

To a stirred solution of **La** (0.77 g, 2.5 mmol) in dry methylene chloride (30 mL), $NiBr_2$(DME) (2.5 mmol, 0.77 g) was added, and the reaction mixture was stirred at ambient temperature for 24 h. The resultant dark-purple solution was filtrated to get rid of the possible insoluble impurities, and then the filtrate was concentrated to a volume of 1–20 ml under vacuum. *n*-Hexane was added to precipitate the product. The blue-purple precipitate was filtered, washed repeatedly with *n*-hexane and dried under vacuum (yield: 1.11 g, 84%). Found: C, 47.94; H, 5.38; N, 5.47. Anal. Calc. (C21H28Br2N2Ni): C, 47.86; H, 5.36; N, 5.32; ^1H NMR ($CDCl_3$) (ppm): 176.99 (6H, N–$(CH_3)_2$), 28.55 (1H,–CH=N–), 21.39 (2H, m-Ar-aniline), 16.39 (1H, 3-Ar-backbone), 7.72 (–CH(isopropyl), broden peak), 3.93 and 2.82 (6H and 6H, –CH_3(isopropyl)), 1.68 (6-Ar-backbone, overlapped peak), −6.69 (1H, 4-Ar-backbone), −8.56 (1H, 5-Ar-backbone), −13.51 (1H, p-Ar-aniline).

4.2.4. ((2,6-dimethyl)Phenyl-N=CH-C_6H_4-o-N(Me)$_2$)$NiBr_2$ (*B*)

By using the similar procedure described for complex **A**, complex **B** was obtained as purple solid in 87% yield. Found: C, 43.43; H, 4.32; N, 6.08. Anal. Calc. ($C_{17}H_{20}Br_2N_2Ni$): C, 43.36; H, 4.28; N, 5.95; ^1H NMR ($CDCl_3$) (ppm): 175.29 (6H, N-$(CH_3)_2$), 28.61 (1H, –CH=N–), 26.24 (6H, CH_3–Ar-aniline), 21.44 (2H, m-Ar-aniline), 16.95 (1H, 3-Ar-backbone), 1.76 (1H, 6-Ar-backbone), −6.86 (1H, 4-Ar-backbone), −9.06 (1H, 5-Ar-backbone), −14.92 (1H, p-Ar-aniline).

4.3. X-ray diffraction measurements

The crystal data for complex **B** were collected on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å) at 296(2) K. Crystal structure was solved by direct methods with SHELXS-97 [45]. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [46]. The final agreement factor values are $R_1 = 0.0412$, $wR_2 = 0.0995$. Crystal data and structure refinement details for complex **B** are summarized in Table 2.

4.4. Norbornene polymerization

A typical polymerization procedure was carried out in a 50 ml round-bottom glass flask, which was equipped with a magnetic stirring bar and thoroughly dried by heating under vacuum. The desired amounts of methylaluminoxane (dissolved in 9 ml toluene) and norbornene solution (10 ml, 4.0 mol/L) were added into the flask via syringe. The system was allowed to equilibrate at the selected temperature for 20 min with stirring. Then, the desired amount of precursor (dissolved 1 ml toluene) was added into the flask to start the polymerization. The reaction mixture was continuously stirred at the selected temperature for 30 min. Then, polymerization was terminated by adding acidic ethanol (20 ml, ethanol/HCl: 95/5). The white precipitate was filtered, washed repeatedly with ethanol and dried under vacuum at 60 °C to a constant weight.

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Appendix ASupplementary material

The supplementary data associated with this article can be found in the online version at doi:10.1016/j.jorganchem.2011.08.017. CCDC 824799 contains the supplementary crystallographic data for complex **B**. This data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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