

Nickel (II) complexes with β -enaminoketonato chelate ligands: Synthesis, solid-structure characterization and reactivity toward the addition polymerization of norbornene

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Abstract

Based on two β -enaminoketonato ligands [ArNC(CH₃)C(H)C(CF₃)OH] (**L**₁, Ar = 2,6-Me₂C₆H₃; **L**₂, Ar = 2,6-*i*-Pr₂C₆H₃), their mono(β -enaminoketonato)nickel (II) complexes [(ArNC(CH₃)C(H)C(CF₃)O)Ni(Ph)(PPh₃)] (**1**, Ar = 2,6-Me₂C₆H₃; **3**, Ar = 2,6-*i*-Pr₂C₆H₃) and bis(β -enaminoketonato)nickel (II) complexes [(ArNC(CH₃)C(H)C(CF₃)O)₂Ni] (**2**, Ar = 2,6-Me₂C₆H₃; **4**, Ar = 2,6-*i*-Pr₂C₆H₃) have been synthesized and characterized. The molecular structures of complex **1**, **2** and **4** have been confirmed by single-crystal X-ray analyses. After being activated with methylaluminumoxane (MAO) these catalytic precursors **1–4** could polymerize norbornene to afford addition-type polynorbornene (PNB). Interestingly, catalytic activities and PNB productivity were greatly enhanced due to the introduction of strong electron-withdrawing group – trifluoro methyl into the ligands. Catalytic activities, polymer yield, M_w and M_w/M_n of PNB have been investigated under various reaction conditions.

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1. Introduction

Olefin addition polymerization is one of the most important processes in industrial and academic chemistry. Although this field typically has been the domain of early-metal catalysts, in the past decade there has been growing interest in late-transition-metal catalysts [1]. Among them, nickel-based catalysts especially neutral nickel catalysts [2,3] play an important role and even are considered to be very promising catalysts for the olefin polymerization and copolymerization. Moreover, nickel-based catalytic systems with ligands of the type O–Y (where Y is N or S) are particularly interesting and have been shown to be very effective catalysts in α -olefin and polar olefin polymerization [4]. Recently, Wu et al. [5] have prepared bis(β -enaminoketonato)nickel (II) complexes and

investigated their catalytic methyl methacrylate polymerization behaviors. Li et al. [6] also synthesized a series of bis(β -enaminoketonato)nickel (II) and mono(β -enaminoketonato)nickel (II) complexes utilizing different nickel sources, and studied their reactivities towards the polymerization of norbornene and copolymerization of ethylene with methyl methacrylate, respectively. As we know that a little variation of the ligand structure may lead to significant changes in the catalytic reactivity, our group have designed and synthesized several series of nickel catalysts supported by [N,O] monoanionic and bisanionic ligands during the past few years [7]. Herein, we introduce strong electron-withdrawing group into the β -enaminoketonato chelate ligands and synthesize their nickel complexes.

Polynorbornene produced by the addition polymerization possesses unique physical and chemical properties [8]. After Deming and Novak introduced the first nickel complex for the addition polymerization of norbornene in 1993 [9], we [7d,10] other groups [11] have found that

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some other nickel complexes also show high catalytic activity toward this polymerization reaction.

In this contribution we synthesized four nickel (II) complexes with β -enaminoketonato chelate ligands and investigated their polymerization behaviors towards norbornene. Experimental results showed that these nickel complexes displayed very high activities for the addition polymerization of norbornene upon activation with methylaluminoxane (MAO) and catalytic activities were greatly enhanced because of the introduction of strong electron-withdrawing group (trifluoro methyl) into the ligands. Especially, the highest polynorbornene productivity was up to 92%, which was different from other reported results [9,11]. Three typical molecular structures of nickel catalysts were characterized by an X-ray crystallographic study.

2. Results and discussion

2.1. Syntheses of ligands and complexes

The syntheses of ligands are outlined in Scheme 1. According to a modified method [12] on the condensation reaction of Schiff-base, we did not obtain the desired β -diketiminato ligands because of the strongly electron withdrawing abilities of trifluoro methyl in 1,1,1-trifluoro-2,4-pentanedione, whereas only got β -enaminoketonato ligand **L**₁ and **L**₂ reported in this contribution. Herein, titanium tetrachloride was employed to induce the reaction to go along successfully in the process of the preparation of ligands. Mechanistically, the titanium atom initially coordinated with the carbonyl oxygen, thereby preparing the carbonyl group for reaction with amines, and finally induced the transfer of the carbonyl oxygen atom from carbon to titanium. Owing to the properties of electron withdrawing of trifluoro methyl group the oxygen atom near to the methyl group was replaced by 2,6-dimethylaniline.

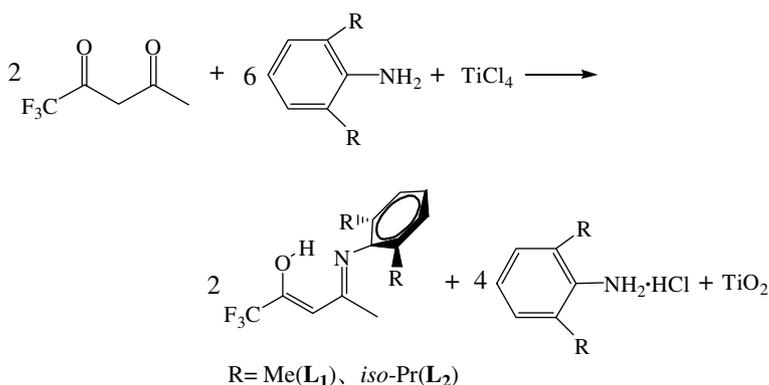
The obtained organic ligands were treated with *n*-BuLi in THF and then reacted with *trans*-chloro(phenyl)bis(triphenylphosphane)nickel (II) to prepare complexes. After lithium salts of ligands were obtained, mono (β -enamino-

ketonato)nickel (II) and bis(β -enaminoketonato)nickel (II) complexes were synthesized, respectively, when the ratio of *trans*-[Ni(PPh₃)₂(Ph)Cl] to ligands were ca. 1:1 and 1:2. In addition, experimental results showed that the complexes **2** and **4** could be also formed from **1** and **3** upon treatment with the lithium salts of ligand anions. All these complexes were all purified by recrystallizing from toluene. The syntheses of the nickel complexes as catalytic precursors are shown in Scheme 2.

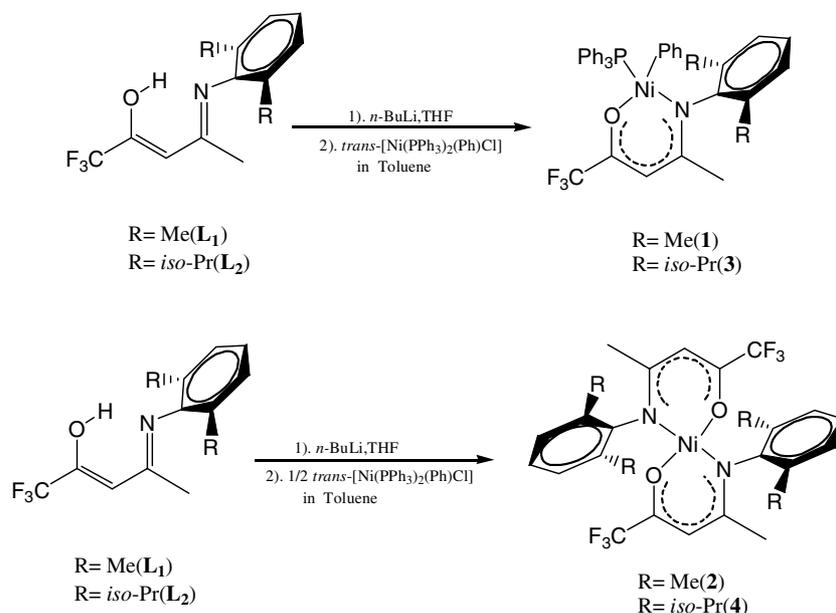
2.2. Structure analyses

Single crystals of complex **1**, **2** and **4** suitable for X-ray diffraction study were grown from a concentrated toluene at -30 °C. The collection data and refinement data of analyses are summarized in Table 1. The ORTEP diagrams of these three complexes are, respectively, shown in Figs. 1–3 with selected bond lengths and angles.

Complex **1** contains a chelating β -enaminoketonato ligand, a triphenylphosphane group (PPh₃) and a phenyl group. The bulky 2,6-dimethylbenzene moiety occupies the position *trans* to PPh₃ with a nearly linear P(1)–Ni(1)–N(1) angle of 170.24(10)°, and the phenyl group attached to Ni lies in a position *trans* to O(1) with a C(14)–Ni(1)–O(1) angle of 165.98(14)°. The *cis* angles at nickel center are in the range of 86.47–93.26°. Thus, the nickel lies perfectly on the square plane defined by the four donor atoms. In addition, the deviation of the metal ion from the plane of [P(1), O(1), N(1) and C(14)] is approximately 0.022 Å. As shown in Figs. 2 and 3, complex **2** has a crystal structure very similar to complex **4**. The anticipated formation of tetrahedral complex was not observed. On the contrary they are both nearly ideal four-coordinate, square-planar configurations in the solid state. In complex **2** the nickel atom deviates from the [N(1), C(1), C(2) C(3) and O(1)] plane about 0.0593 Å. The bulky 2,6-dimethylbenzene rings substituted on the imine moieties are almost perpendicular to the metallacycle plane [Ni, N(1), C(1), C(2) C(3) and O(1)] (dihedral angle ca. 95.9°). The structure of complex **4** is nearly in consistent with reported result [6b].



Scheme 1. Synthesis of ligands.



Scheme 2. Syntheses of nickel complexes.

Table 1
Crystal data and summary of data collection and refinement details for **1**, **2** and **4**

Formula	$\text{C}_{37}\text{H}_{33}\text{F}_3\text{NNiOP}$	$\text{C}_{26}\text{H}_{26}\text{F}_6\text{N}_2\text{NiO}_2$	$\text{C}_{34}\text{H}_{42}\text{F}_6\text{N}_2\text{NiO}_2$
Formula weight	654.32	571.20	683.40
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	$Pna2_1$	$P\bar{1}$	$P\bar{1}$
a (Å)	25.810(7)	7.687(13)	8.674(4)
b (Å)	13.568(4)	7.968(13)	8.878(4)
c (Å)	9.117(2)	11.085(18)	11.576(5)
α (°)	90	76.78(2)	77.559(5)
β (°)	90	79.04(2)	82.785(6)
γ (°)	90	79.89(2)	81.712(6)
V (Å ³)	3192.6(14)	642.7(18)	857.3(6)
Z	4	2	2
Color	Red	Red-orange	Red-orange
Crystal size (mm)	0.20 × 0.10 × 0.08	0.25 × 0.20 × 0.15	0.15 × 0.10 × 0.08
D_{calc} (g cm ⁻³)	1.361	1.476	1.324
μ (mm ⁻¹)	0.706	0.824	0.630
θ Limits (°)	1.58/26.01	1.91/25.01	1.81/25.01
Radiation ($\lambda/\text{Å}$)	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)
$F(000)$	1360	294	358
Number of observed reflections	6043	2220	2987
Number of parameters refined	400	167	210
R_1 [$I > 2\sigma(I)$]	0.0451	0.0562	0.0457
wR_2 (all data)	0.0975	0.1321	0.1258
Goodness-of-fit on F^2	1.065	1.039	1.104

2.3. Addition polymerization of norbornene

For **1–4**, preliminary catalytic studies revealed remarkably high activities in the presence of MAO for the addition polymerization of norbornene. In no case has polynorbornene (PNB) been obtained using **1–4** in the absence of aluminium cocatalyst, whilst the use of up to 5000 equivalents of MAO in the absence of any nickel species, under the polymerization conditions employed here, afforded only negligible polymer. The norbornene polymerization

results are collected in Table 2. In general, the steric structure and bulky group in nickel complexes slightly influence their catalytic activities. Complex **1**, bearing 2,6-dimethylbenzene group, displays higher catalytic activities than complex **3**, with bulkier 2,6-diisopropylbenzene, at the same polymerization conditions. Mechanistically [11f, 11h], the bulkier 2,6-diisopropylbenzene group of complex **3** makes the insertion of norbornene into Ni–C bond more difficult than 2,6-dimethylbenzene of complex **1**. Thus, complex **3** displays lower catalytic activity than complex

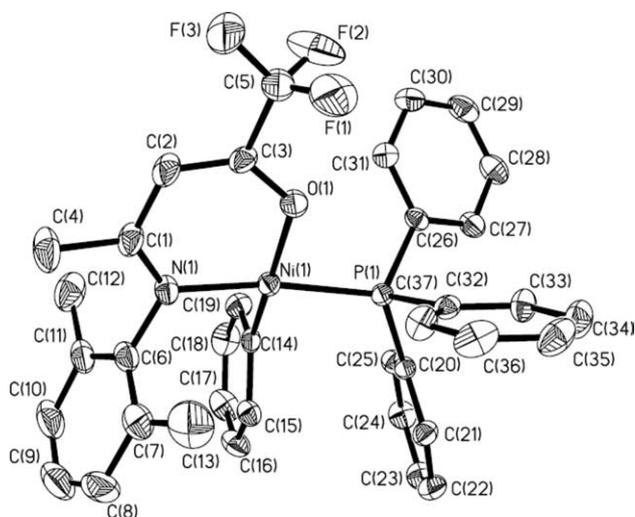


Fig. 1. Molecular structure of complex 1. Selected bond lengths (Å) and angles (°): Ni(1)–C(14) = 1.889(3), Ni(1)–O(1) = 1.915(2), Ni(1)–N(1) = 1.950(3), Ni(1)–P(1) = 2.1899(10), C(14)–Ni(1)–O(1) = 165.98(14), C(14)–Ni(1)–N(1) = 92.89(13), O(1)–Ni(1)–N(1) = 93.26(11), C(14)–Ni(1)–P(1) = 86.47(10), O(1)–Ni(1)–P(1) = 89.56(7), N(1)–Ni(1)–P(1) = 170.24(10).

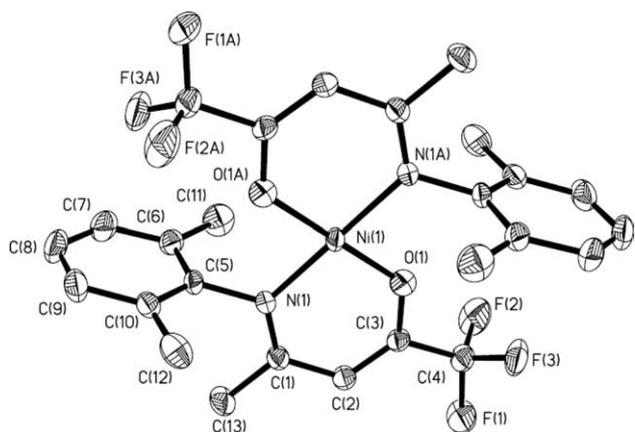


Fig. 2. Molecular structure of complex 2. Selected bond lengths (Å) and angles (°): Ni(1)–O(1) = 1.826(4), Ni(1)–O(1A) = 1.826(4), Ni(1)–N(1A) = 1.922(4), Ni(1)–N(1) = 1.922(4), O(1)–Ni(1)–O(1A) = 180.00(17), O(1)–Ni(1)–N(1A) = 87.48(16), O(1A)–Ni(1)–N(1A) = 92.52(16), O(1)–Ni(1)–N(1) = 92.52(16), O(1A)–Ni(1)–N(1) = 87.48(16), N(1A)–Ni(1)–N(1) = 180.000(1).

1. As seen from the polymerization data in Table 2, the activities of complex 2 are very near to those of complex 1. Similarly, the activities of 4 are near to 3. These results may be due to the similar polymerization mechanism in the presence of excess MAO between mono(β -enaminoketonato)nickel (II) and bis(β -enaminoketonato)nickel (II) complexes at the same polymerization conditions.

To investigate the reaction parameters affecting addition polymerization of norbornene, the catalytic precursor 1 was studied under different reaction conditions. Varying the MAO:1 ratio (expressed here as Al:Ni ratio) had considerable effects on catalytic activity and M_w , as shown in Table 3. When Al:Ni is not more than 2000 (entry 1, Table

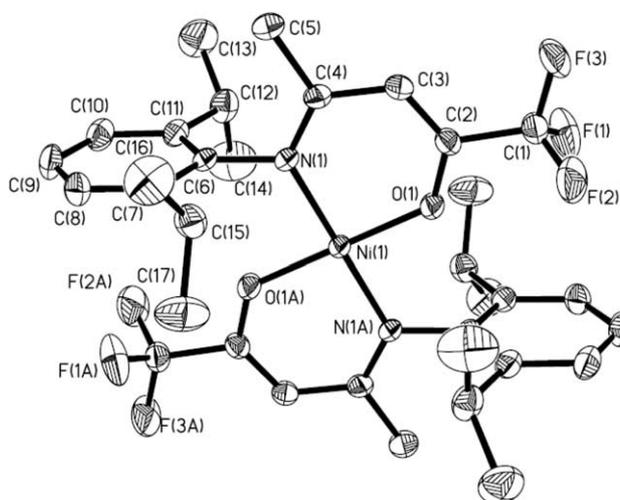


Fig. 3. Molecular structure of complex 4. Selected bond lengths (Å) and angles (°): Ni(1)–O(1A) = 1.837(2), Ni(1)–O(1) = 1.837(2), Ni(1)–N(1A) = 1.932(2), Ni(1)–N(1) = 1.932(2), O(1A)–Ni(1)–O(1) = 180.00(17), O(1A)–Ni(1)–N(1A) = 92.52(9), O(1)–Ni(1)–N(1A) = 87.48(9), O(1A)–Ni(1)–N(1) = 87.48(9), O(1)–Ni(1)–N(1) = 92.52(9), N(1A)–Ni(1)–N(1) = 180.00(13).

Table 2

Addition polymerization of norbornene with nickel complexes 1–4 activated by methylaluminoxane (MAO)^a

Entry	Complex	Polymer (g)	Activity ^b	M_w^c	M_w/M_n^c
1	1	1.74	5.22	2.82	2.43
2	2	1.72	5.16	2.75	2.54
3	3	1.56	4.68	2.73	2.62
4	4	1.51	4.53	3.93	3.22

^a Polymerization conditions: solvent, chlorobenzene; total volume, 10 mL; nickel complex, 0.2 μ mol; norbornene, 1.88 g [norbornene/nickel(molar) = 100000]; 0.66 mL of MAO (1.51 M) [Al/Ni = 5000]; reaction time, 10 min; temperature, 30 °C.

^b 10^7 g PNB \cdot mol⁻¹Ni \cdot h⁻¹.

^c M_w (10^6 g mol⁻¹) and M_w/M_n values were determined by GPC.

Table 3

Influence of the MAO amount on the activities of complex 1

Entry	Amount of MAO (equiv.)	Yield (%)	Activity ^a	M_w^b	M_w/M_n
1	2000	–	–	–	–
2	2500	14.6	0.822	2.69	9.99
3	3000	72.7	4.11	4.86	5.62
4	4000	78.1	4.41	1.18	5.31
5	5000	92.2	5.22	2.82	2.43
6	6000	90.0	5.09	2.28	8.26
7	10000	87.2	4.92	1.05	5.13

^a 10^7 g PNB \cdot mol⁻¹Ni \cdot h⁻¹.

^b M_w (10^6 g mol⁻¹). Polymerization conditions: solvent, chlorobenzene; total volume, 10 mL; nickel complex, 0.2 μ mol; norbornene, 1.88 g [norbornene/nickel(molar) = 100000]; temperature, 30 °C; reaction time, 10 min.

3), the obtained polymer is negligible. The entry 2 in Table 3 showed that the activity is only up to 10^6 g PNB \cdot mol⁻¹Ni \cdot h⁻¹ when using up to 2500 equivalents

of MAO. However, the catalytic activity exceeds 10^7 g PNB · mol⁻¹Ni · h⁻¹ when Al:Ni > 3000. Moreover, the activity is highest at Al:Ni = 5000 and at the same point the highest PNB productivity (up to 92%) was also observed.

Table 4 reveals the effects of reaction temperature on catalytic activities and M_w . With increasing reaction temperature, the catalytic activities first increase and then decrease – the highest activity is at 30 °C (5.22×10^7 g PNB · mol⁻¹Ni · h⁻¹). On the contrary, M_w always decrease with increasing temperature.

Fig. 4 shows the X-ray diffraction (XRD) spectra of the obtained PNB. The spectra display two broad halos at 2θ of ca. 11° and 18° that can be attributed to a short range order, or pseudo-periodicity of the arrangement of the bicycle units along the chain. This is almost in agreement with the results reported by our and other groups [10,13]. No traces of Bragg reflections are revealed at crystalline regions. Therefore, the PNB herein is amorphous.

The polymer obtained was characterized by IR, ¹H NMR, ¹³C NMR and DSC analyses. All IR spectra, ¹H NMR spectra and ¹³C NMR spectra (see Fig. 5) were similar and characteristic of addition-type PNB, and revealed no traces of double bonds that are typical for ROMP (ring-opening metathesis polymerization) PNB [14,11h].

Table 4
Influence of the reaction temperature (T) on the activities of complex 1

Entry	T (°C)	Yield (%)	Activity ^a	M_w ^b	M_w/M_n
1	0	62.3	3.52	2.92	1.73
2	30	92.2	5.22	2.82	2.43
3	60	71.6	4.04	2.69	1.82
4	90	31.3	1.77	2.61	2.22

Polymerization conditions: solvent, chlorobenzene; total volume, 10 mL; nickel complex, 0.2 μmol; norbornene, 1.88 g [norbornene/nickel (molar) = 100000]; Al/Ni = 5000; reaction time, 10 min.

^a 10^7 g PNB · mol⁻¹Ni · h⁻¹.

^b M_w (10^6 g mol⁻¹).

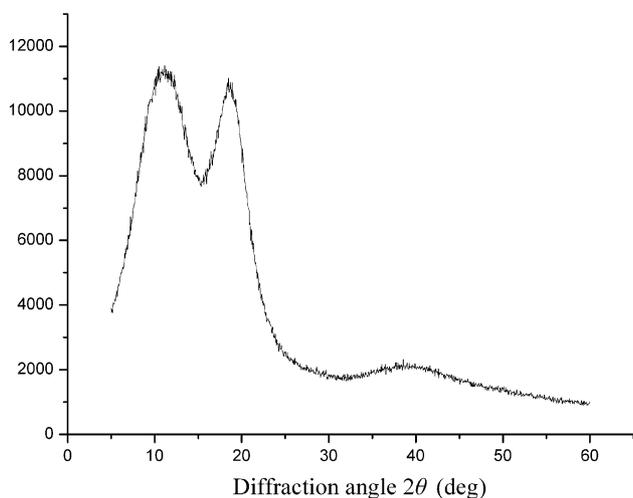


Fig. 4. XRD diagram of PNB.

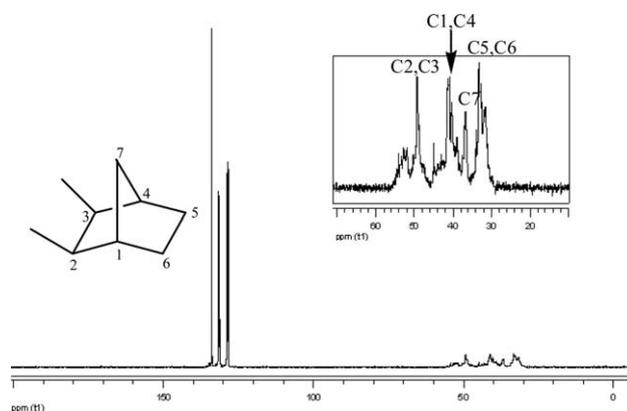


Fig. 5. ¹³C NMR spectra of PNB.

Our attempts to determine the glass transition temperature (T_g) of PNB failed, and the differential scanning calorimetric (DSC) studies did not give an endothermic signal upon heating to the decomposition temperature (above 450 °C).

3. Conclusion

We have synthesized mono(β-enaminoketonato)nickel (II) and bis(β-enaminoketonato)-nickel (II) complexes 1–4 and characterized three typical molecular structures of complex 1, 2 and 4 by an X-ray crystallographic study. The experimental results showed that all these complexes displayed extremely high catalytic activities to the addition polymerization of norbornene after being activated with MAO. The catalytic activities of up to 5.22×10^7 g PNB · mol⁻¹Ni · h⁻¹ and M_w up to 4.86×10^6 g mol⁻¹ were observed. Activities, polymer yield and M_w could be controlled by the variation of reaction parameters. Interestingly, catalytic activities and PNB productivity were greatly enhanced because of the introduction of strong electron-withdrawing group (trifluoro methyl) into the ligands. The PNB obtained here are amorphous and soluble in halogenated aromatic hydrocarbons. A study on syntheses and polymerization behaviors of mono(β-diketiminato)nickel (II) complexes bearing trifluoro methyl group is our current investigation.

4. Experimental

4.1. General considerations

All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen using standard Schlenk and vacuum-line techniques. Solvents were dried by refluxing with appropriate drying agents and distilled under nitrogen prior to use. *trans*-[Ni(PPh₃)₂(Ph)Cl] were prepared according to the literature procedures [15]. 1,1,1-Trifluoro-2,4-pentanedione (98%) was purchased from ACROS. Norbornene (bicyclo[2.2.1]hept-2-ene, Acros) was purified by distillation over sodium and used as a chlorobenzene solution. MAO was purchased from

Aldrich as 10% weight of a toluene solution and used without further purification. Other commercially available reagents were purchased and used without purification.

¹H NMR spectra were recorded with a Varian Unity-400 spectrometer. Elemental analyses were performed on an Elementar vario EL III Analyzer. FT-IR analyses were detected with a Nicolet-FT-IR-50X spectrometer. NMR data for PNB were obtained at ambient temperature on Bruker AC 500 spectrometer instruments using *o*-chlorobenzene-*d*₄ as a solvent. Average molecular weight (*M*_w) and molecular weight distribution (*M*_w/*M*_n) values of PNB products were determined using a PL GPC-220 gel permeation chromatograph at 150 °C using a narrow standards calibration and equipped with three PL gel columns (sets of PL gel 10 m MIXED-B LS). Trichlorobenzene was employed as a solvent at a flow rate of 1.00 mL/min. DSC measurements were performed with a Perkin-Elmer Pyris 1 DSC. The XRD diagram of the polymer powder 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°.

4.2. Ligand and complex synthesis

4.2.1. ((2,6-Me₂C₆H₃)NC(CH₃)C(H)C(CF₃)OH) (L₁)

1,1,1-Trifluoro-2,4-pentanedione (2.0 mL, 16.48 mmol) was placed in a three neck flask with 52.19 mmol (6.45 mL) of anhydrous 2,6-dimethylaniline dissolved in 20 mL of toluene at -10 °C. Then 1.0 mL of TiCl₄ (9.07 mmol) dissolved in ca. 8 mL of toluene was added dropwise. The material turned dark brown. After permitting the reaction mixture to warm to room temperature, the material was heated at 90 °C for 10–12 h, cooled, allowed to stand overnight, filtered, and the salt cake washed with more toluene. After removing solvent from the combined filtrate and wash, the residue was passed down a short alumina column eluting with hexane. Evaporating the hexane, the product was isolated as yellow oil. Yield: 2.76 g, 10.71 mmol, 65%. ¹H NMR (CDCl₃): δ = 12.10 (s, 1H, O-H), 7.14 (m, 3H, Ph-H), 5.56 (s, 1H, C-H_{backbone}), 2.16 (s, 6H, Ph-CH₃), 1.79 (s, 3H, -CH₃).

4.2.2. ((2,6-*i*-Pr₂C₆H₃)NC(CH₃)C(H)C(CF₃)OH) (L₂)

The synthesis of ligand L₂ was carried out as described for ligand L₁. Yield: 3.56 g, 11.37 mmol, 69%. ¹H NMR (CDCl₃): δ = 12.20 (s, 1H, O-H), 7.36 (t, 1H, Ph-H), 7.22 (d, 2H, Ph-H), 5.56 (s, 1H, C-H_{backbone}), 2.93 (m, 2H, *i*-Pr-CH), 1.81 (s, 3H, -CH₃), 1.27–1.16 (dd, 12H, *i*-Pr-CH₃).

4.2.3. ((2,6-Me₂C₆H₃)NC(CH₃)C(H)C(CF₃)O)Ni(Ph)-(PPh₃) (1)

A solution of ligand L₁ (0.257 g, 1.0 mmol) in THF (15 mL) was cooled to -78 °C, and 1.1 equiv. of *n*-BuLi was added dropwise (0.48 mL, 2.3 M, 1.1 mmol). The mixture was warmed to room temperature by itself and stirred for 2 h to afford the lithium salt of the ligand L₁. After

evaporation of THF under vacuum, the lithium salt of L₁ was dissolved in 10 mL of toluene. Then the solution containing the lithium salt of L₁ was slowly channeled into a 50 mL flask with 0.668 g of *trans*-[Ni(PPh₃)₂(Ph)Cl] (0.96 mmol) in 10 mL of toluene and continuously stirred overnight at room temperature. The reaction mixture was separated by centrifugation to remove LiCl. After the upper clear dark red solution was concentrated to about 3 mL, 20 mL of hexane was added and complex 1 was obtained as a red-orange solid. Yield: 0.446 g, 71%. Red single crystals suitable for X-ray analysis were recrystallized from toluene at -30 °C. Anal. Calc. for C₃₇H₃₃NOPF₃Ni (654.32): C, 67.92; H, 5.08; N, 2.14. Found: C, 68.18; H, 5.14; N, 1.97%. ¹H NMR (CDCl₃): δ = 7.41–7.00 (m, 23H, Ph-H), 5.36 (s, 1H, C-H_{backbone}), 2.10 (s, 6H, Ph-CH₃), 1.71 (s, 3H, -CH₃).

4.2.4. ((2,6-Me₂C₆H₃)NC(CH₃)C(H)C(CF₃)O)₂Ni (2)

Complex 2 was prepared in a manner similar to that for complex 1, but the ratio of *trans*-[Ni(PPh₃)₂(Ph)Cl] to L₁ was ca. 1:2, instead of 1:1. Yield: 0.335 g, 61%. Red-orange single crystals suitable for X-ray were recrystallized from toluene at -30 °C. Anal. Calc. for C₂₆H₂₆N₂O₂F₆Ni (571.20): C, 54.67; H, 4.59; N, 4.90. Found: C, 54.88; H, 4.90; N, 5.11%. ¹H NMR (CDCl₃): δ = 7.00–6.90 (m, 6H, Ph-H), 5.14 (s, 2H, C-H_{backbone}), 2.59 (s, 12H, Ph-CH₃), 1.44 (s, 6H, -CH₃).

4.2.5. ((2,6-*i*-Pr₂C₆H₃)NC(CH₃)C(H)C(CF₃)O)Ni(Ph)-(PPh₃) (3)

Complex 3 was obtained as dark red powder in a yield of 68%, 0.464 g. Anal. Calc. for C₄₁H₄₁NOPF₃Ni (710.44): C, 69.32; H, 5.82; N, 1.97. Found: C, 69.71; H, 5.54; N, 1.91%. ¹H NMR (CDCl₃): δ = 7.67–6.45 (m, 23H, Ph-H), 5.77 (s, 1H, C-H_{backbone}), 3.72–3.69 (m, 2H, *i*-Pr-CH), 1.60 (s, 3H, CN-CH₃), 1.31–1.14 (dd, 12H, *i*-Pr-CH₃).

4.2.6. ((2,6-*i*-Pr₂C₆H₃)NC(CH₃)C(H)C(CF₃)O)₂Ni (4)

Complex 4 was obtained as dark red powder in a yield of 57%, 0.374 g. Red-orange single crystals suitable for X-ray were recrystallized from toluene at -30 °C. Anal. Calc. for C₃₄H₄₂N₂O₂F₆Ni (683.40): C, 59.76; H, 6.19; N, 4.10. Found: C, 60.04; H, 6.08; N, 3.93%. ¹H NMR (CDCl₃): δ = 7.16–7.02 (m, 6H, Ph-H), 5.35 (s, 2H, C-H_{backbone}), 3.78 (m, 4H, *i*-Pr-CH), 1.54 (dd, 24H, *i*-Pr-CH₃), 1.21 (s, 6H, CN-CH₃).

4.3. Structure solution and refinement for complex 1, 2, and 4

For complexes 1, 2, and 4, a single crystal suitable for X-ray analysis was sealed into a glass capillary, and the intensity data of the single crystal were collected on the CCD-Bruker Smart APEX system. All determinations of the unit cell and intensity data were performed with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All data were collected at room temperature using the ω scan

technique. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were included but not refined. Crystallographic data are summarized in Table 1.

4.4. Polymerization of norbornene

In a typical procedure (entry 5, Table 3), 0.2 μmol of nickel complex **1** in 1.0 mL of chlorobenzene, 1.88 g of norbornene in 3.0 mL of chlorobenzene and another 3.0 mL fresh chlorobenzene were added into a special polymerization bottle (20 mL) with a strong stirrer under nitrogen atmosphere. After the mixture was kept at 30 °C for 10 min, 0.35 mL of MAO was charged into the polymerization system via syringe and the reaction was initiated. Ten minutes later, the acidic ethanol ($V_{\text{ethanol}}:V_{\text{concd.HCl}} = 20:1$) was 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 10.0 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} . ^1H NMR: δ 0.7–3.0 (m, maxima at 1.29 1.71 2.05 2.36 ppm).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 276323–276325 for compound **1**, **2** and **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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