行政院國家科學委員會專題研究計畫 期中進度報告

含胺 - 亞胺配基的化學(1/3)

<u>計畫類別</u>: 個別型計畫 <u>計畫編號</u>: NSC92-2113-M-002-025-<u>執行期間</u>: 92 年 08 月 01 日至 93 年 07 月 31 日 執行單位: 國立臺灣大學化學系暨研究所

計畫主持人: 陳竹亭

<u>計畫參與人員</u>:楊豐兆、李虹儀、林雅淇、管仕豪、陳宜君、楊志璁、張益信、 王哲峻

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<u>報告附件</u>:出席國際會議研究心得報告及發表論文 處理方式:本計畫可公開查詢

中 華 民 國 93 年 5 月 28 日

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摘要

Olefin polymerization and co-polymerization catalyzed by Ni(II) complexes that bear new bidentate ligands with coordinating functionalities of amine and imine are succeeded. A class of new α -aminoaldeimines R₂NCMe₂CH=N(2,6-R'₂C₆H₃) (R = Me R' = ⁱPr (L2-1d), $R = Et R' = H (L2-2a), Me (L2-2b), Et (L2-2c), {}^{i}Pr (L2-2d), R = {}^{n}Pr R' = {}^{i}Pr (L2-3d), R_{2} =$ $c-C_4H_8$ R' = Ph (L2-4a), ⁱPr (L2-4d), R₂ = $c-C_5H_{10}$ R' = Me (L2-5b)) and R₂NCH₂CH= $N(2,6-R'_{2}C_{6}H_{3})$ (R = Et R' = Me (L1-2b), R₂ = c-C₅H₁₀ R' = ⁱPr (L1-5d)) are synthesized. The corresponding nickel complexes $[R_2NCMe_2CH=N(2,6-R'_2C_6H_3)]NiBr_2$ (R = Me R' = ⁱPr (Ni2-1d), R = Et R' = H (Ni2-2a), Me (Ni2-2b), Et (Ni2-2c), ⁱPr (Ni2-2d), $R = {}^{n}Pr R' = {}^{i}Pr$ (Ni2-3d), $R_2 = c-C_4H_8$ R' = Ph (Ni2-4a), ⁱPr (Ni2-4d), $R_2 = c-C_5H_{10}$ R' = Me (Ni2-5b)) and $[R_2NCH_2CH=N(2,6-R'_2C_6H_3)]NiBr_2$ (R = Et R' = Me (L1-2b), R_2 = c-C_5H_{10} R' = ⁱPr (L1-5d)) are prepared. The molecular structures of Ni1-5d, Ni2-1b, Ni2-2b, and Ni2-4d are determined by X-ray crystallography, showing distorted tetrahedral configuration. The SQUID data indicate a ground state of triplet. With the assistance of MAO, the nickel complexes are activated to catalyze ethylene polymerization under moderate pressure and ambient temperature. The activity can reach to 10^3 g PE/mmol Ni·h. The PE products are generally highly branched with $M_n \sim 10^5$ and PDI<2. Catalysis of norbornene polymerization using such nickel complexes is achieved with activity of 10^2 g PN/mmol Ni·h. The reactions of cyclic olefinic co-polymerization of ethylene/norbornene are resulted to give the soluble products of medium M_n (10³), with high norbornene content (ca. 70~90%), and high T_{g} (ca. 220~300 °C). The polymerization of ethylene appears to be facilitated with the steric decrease of the amino substituents, but the opposite correlation is observed for the nobornene polymerization.

The late transition-metal catalysts bearing the designed ligands in constrained geometry used for olefin polymerization are acquiring increasing attention.¹ Such catalysts not only demonstrate promising activity, but also confer the catalytic reactions as well as the polymeric products with characteristic, that is particularly different from those caused by metallocene catalysts of early transition-metals.² Among the studied ligand systems, the bidentates of diimines bearing suitable bulky substituents are proved to be most successful.³

On the other hand, seeking for the bidentates that contain hybrid coordinating functionalities remains a rising field since the study of the SHOP process.⁴ It is generally believed that the asymmetrical ligands potentially enable to afford more controlling features to the reactivity.⁵ Nickel and palladium catalysts with bidentate ligands containing phosphorus and nitrogen donors are found to facilitate CO-ethylene copolymerization,⁶ however are generally unsatisfactory to ethylene polymerization. In contrast, the bidentates with hard hybrid donors, such as Shiff base derivatives, have shown potential toward olefin polymerization.⁷ To our surprise, the bidentates comprising amine and imine are hardly explored in the broad regime of catalysis.⁸ We herein report the first example of nickel catalysts bearing new amine-imine bidentate ligands, which exhibit high reactivity to the polymerization and copolymerization of olefins. The different aza-functionalities can convey individual influence to the polymerization reactions.

New α -amino-aldeimines in the form of R₂NCMe₂CH=N(2,6-R'₂C₆H₃) (L) are synthesized via a route first by amination of α -bromoaldehyde, then followed by condensation with aniline derivatives as shown in Scheme I.⁹ The substitution reactions of

Scheme I



(DME)NiBr₂ (DME =1,2-dimethoxyethane) with L generate the corresponding neutral complexes [R'₂NCMe₂CH=N(2,6-R₂C₆H₃)]NiBr₂ (R = Me R' = ⁱPr (1a), R = Et R' = ⁱPr (2a), Me (2b), H (2c), R = ⁿPr R' = ⁱPr (3a), R = c-C₄H₈ R' = ⁱPr (4a)) in ca. 60% yields (Scheme II). Similarly, an α -aminoketimine Et₂NCH₂CMe=N(2,6-Me₂C₆H₃) (L5b) and its dibromo nickel complex 5b are also prepared.



The violet dibromonickel complexes with L are generally soluble in CH_2Cl_2 or $CHCl_3$, and suffer hydrolysis or deterioration while dissolving under ambient conditions. In some cases, the NMR spectra are severely interfered by paramagnetism of the samples. The SQUID measurement for **2a** indicates a ground state of triplet for such species.

The single-crystals of **2b** and **5b** are grown from CH_2Cl_2/Et_2O . Their molecular structures in distorted tetrahedral geometry are revealed by X-ray crystallographic analysis. Their ORTEP drawings are shown in Figure 1. The distances for the Ni-N1(*sp*³) and the Ni-N2(*sp*²) bond are 2.080(3) and 1.991(3) Å, respectively, for **2b**; 2.045(3) and 2.002(3) Å, respectively, for **5b**. The N1-Ni-N2 angles in **2b** and **5b** are identical, being 82.6(1)° and are comparable with those in the diimine nickel catalysts.¹⁰

The title complexes are found to be active catalysts for ethylene polymerization with the activation of methylaluminum oxide (MAO). The data of polymerization are collected in Table 1. At the pressure of 250 psi and 25 °C, the TOF can reach to $2x10^5$ g/mol Ni·h. The is no noticeable temperature change during the course of the catalytic reactions. In general, the PE products have M_n of 10^5 with most of the dispersity index less than 2. T_g of PE are in the region of -40~-50 °C and T_m about -15~-25 °C. TGA shows less than 10% weight loss until 390 °C. The numbers of branches are in the region of 100~150 per 1000 carbon, which are higher than the previous results of diimine-nickel catalysts.

In contrast to metallocene catalysts that are generally inefficient to polymerize norbornene, it is found such nickel complexes catalyze polymerization of norbonene as well as of ethylene. Norbornene concentration significantly assists the PN formation. The PN products are white insoluble solid with T_g over 350 °C and decompose at 400 °C. Again, the reactivity slightly increases with bulky imino substituent as shown in entries 12-14. The

different amine effect between ethylene polymerization and norbornene polymerization is under investigation.

The studies for copolymerization of ethylene and norbornene catalyzed by the amine-imine nickel complexes exhibit reactivity to 2500 Kg/mol Ni·h under mild conditions. The resulting products of cyclic olefinic copolymers (COC) have medium molecular weight (10^3), excellent solubility in organic solvents, and high norbornene composition () which gives rise to T_g over 300 °C (Table 2).

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entry	catalyst	monomer	$\frac{[Al]}{[Ni]}$	T _{rxn}	yield	activity ^a	M_n^{b}	PDI	branches
	(µmol)			(h)	(g)				per 1000C
1	Ni1-1d (41) ^a	E (400 psi)	480	2	2.91	35.5	42611	1.23	97
2	Ni2-1b (41) ^a	E (200 psi)	480	1/6	2.28	334	236000	1.38	62
3	Ni2-1b (41) ^a	E (250 psi)	480	1/6	3.18	516	279000	1.35	121
4	Ni2-1b (41) ^a	E (300 psi)	480	1/6	5.79	890	404000	1.17	109
5	Ni2-1b (41) ^a	E (350 psi)	480	1/6	7.04	1030	291000	1.32	112
6	Ni2-1b (41) ^a	E (400 psi)	480	1/6	7.56	1106	226,000	1.66	78
7	Ni2-1d (39) ^a	E (400 psi)	480	1/6	7.05	1085	356000	1.21	112
8	Ni2-1d (43) ^a	E (400 psi)	480	0.5	25.5	1186	378,000	1.44	138
9	Ni2-2a (22) ^a	E (250 psi)	480	3	0.58	8.8	12,000	1.88	152
10	Ni2-2b (22) ^a	E (250 psi)	480	3	6.44	97.5	164,000	1.31	149
11]	E (250 psi)	480	24	13.2	25	393,000	1.23	118
12	Ni2-2d (22) ^a	E (100 psi)	480	3	0.48	7.3	119,000	1.19	156
13]	E (150 psi)	480	3	1.01	15.3	165,000	1.19	149
14]	E (250 psi)	480	3	3.44	52.1	238,000	1.69	143
15	Ni2-3d (22) ^a	E (250 psi)	480	3	4.90	74.2	108,000	2.58	103
16	Ni2-4d (22) ^a	E (250 psi)	480	3	10.8	164	252,000	1.47	79
17	Ni2-1d (22) ^b	N (53 mmol)	480	2	0.86	19.5			
18	Ni2-2a (22) ^b	N (53 mmol)	230	0.25	0.86	156			
19	Ni2-2b (22) ^b	N (53 mmol)	230	0.25	1.20	218			
20	Ni2-2d (22) ^b	N (53 mmol)	230	0.25	1.90	345			
21]	N (75 mmol)	230	0.25	2.36	429			
22]	N (100 mmol)	230	0.25	3.53	642			
23	Ni2-3d (22) ^b	N (53 mmol)	480	1	3.46	157			

Table 1Data of Polymerization

^aconditions for ethylene polymerization: 100 mL toluene at 25 °C; ^b conditions for norbornene

polymerization: 6 mL MAO, magnet stirring in 100 mL toluene at 25 °C; ^cdetermined in toluene; ^ddetermined by NMR integration.

entr	ry catalyst	E	Ν	$\frac{[Al]}{[Ni]}$	T _{rxn}	yield	activity	$M_n^{\ b}$	PDI	Tg	N%
	(µmol)	(psi)	(g)		(h)	(g)				(°C)	
1	Ni2-1d (22.0	0) 300	22.5	1035	0.5	1.74	158	3,865	1.96	308	91
2	Ni2-2a (13.5	5) 300	22.5	1035	1.0	1.13	83.7	2,004	3.05	224	77
3	Ni2-2b (13.5	5) 300	22.5	1035	1.0	2.18	161	1,807	3.66	249	73
4	Ni2-2d (13.5	5) 300	22.5	1035	1.0	3.10	230	1,609	3.27	234	75
5	Ni2-2d (13.5	5) 300	50.0	1035	1.0	8.44	625	2,503	2.57	267	82
6	Ni2-3d (22.0	0) 300	22.5	1035	0.5	4.20	382	1,307	2.82	233	73

Table 2Data of copolymerization

Figure 1 ORTEP drawing with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg), (a) for **2b**: Ni-N1 2.080(3), Ni-N2 2.241(4), Ni-Br1 2.3667(6), Ni-Br2 2.3513(6), N1-C1 1.537(5), N2-C2 1.269(4); N1-Ni-N2 82.6(1), Br1-Ni-Br2 118.33(2), C1-N1-Ni 103.3(2), C2-N2-Ni 112.4(2), N1-C1-C2 105.8(3), N2-C2-C1 120.9(3), C3-N2-Ni 127.6(2), C13-N1-Ni 106.7(2), C15-N1-Ni 109.5(2). (b) for **5b**: Ni-N1 2.002(3), Ni-N2 2.045(3), Ni-Br1 2.3749(7), Ni-Br2 2.3381(7), N1-C1 1.266(5), N2-C2 1.489(5); N1-Ni-N2 82.6(1), Br1-Ni-Br2 120.22(3), C1-N1-Ni 114.0(3), C2-N2-Ni 103.5(2), N1-C1-C2 116.5(4), N2-C2-C1 111.1(3), C4-N1-Ni 125.1(2), C12-N2-Ni 114.2(2), C14-N2-Ni 107.7(2).

Experimental Section

General Procedures.

Commericially available reagents were purchased and used without further purification unless otherwise indicated. Toluene and diethyl ether were distilled from purple solutions of benzophenone ketyl under nitrogen, and methylene dichloride was dried over P2O5 and distilled immediately prior to use. Air-sensitive material was manipulated under a nitrogen atmosphere in a glove box or by standard Shlenk techniques. The IR spectra were recorded on a Bio-Rad FTS-40 spectrophotometer. The NMR spectra were measured on a Bruker AC-300 or a Bruker AC-400 spectrometer. The corresponding frequencies for ¹³C NMR spectra were 75.469, and 125.76 Hz MHz, respectively. Values upfield of ¹H and ¹³C data are given in ppm (δ) relative to tetramethylsilane (δ 0.00) in CDCl₃. Mass spectrometric analyses were collected on a JEOL SX-102A spectrometer. Elemental analysis was done on a Perkin-Elmer 2400 CHN analyzer. Gel permeation chromatography (GPC) was performed in toluene at 25 °C using a Kratos model spectroflow 400 equipped with PL-mixed D exclusion limit 400k columns. Differential scanning calorimetry was performed under a continuous nitrogen purge (20 mL/min) on a Pyris 6 DSC Perkin-Elmer instrument. Data were gathered on the third heating cycle using a heating and cooling scan rate of 10-15 °C/min. Thermogravimetric analysis was carried out using a TA Instruments TGA 5100 thermogravimetric analyzer with a heating rate of 10°C/min from 0°C to 800°C under a continuous nitrogen purge.

Synthesis and Characterization.

Me₂NCH₂CH=N(2,6--ⁱPr₂C₆H₃) (L1-1d). To a solution of Me₂NCH₂C(O)OEt (1.31g, 0.01 mol) in dry toluene (20 mL) was added dropwise DIBAL (1M in hexane)(12 mL, 0.012 mol) under a nitrogen atmosphere at -78°C. After the mixture was stirred at the same temperature for 2 h, 2,6-diisopropylaniline (2.66g, 0.015 mol) was added to the reaction mixture. Stirring was continued for an additional 1h, the cooling bath was removed, and stirring was continued for 12 h. The solvent was removed under *vacuo*. The product was isolated by distillation to give a viscous yellow liquid in 56% yields (1.38 g). IR(KBr) $v_{C=N}$ 1672 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 7.65 (t, J_{H-H} = 4.4 Hz, 1H, HC=N), 7.13-7.06 (m, 3H, C₆H₃), 3.36 (d, J_{H-H} = 4.4 Hz, 2H, CH₂), 2.92 (h, J_{H-H} = 6.9 Hz, 2H, CH(CH₃)₂), 2.39 (s,

6H, NC*H*₃), 1.16 (d, $J_{\text{H-H}}$ = 6.9 Hz, 12H, CH(C*H*₃)₂); ¹³C NMR (CDCl₃, 100.625 MHz): δ 166.0 (CH=N), 148.4, 128-123 (phenyl-C), 64.4 (CH₂), 46.0 (NCH₃), 27.9 (CH(CH₃)₂), 22.5 (CH(CH₃)₂); HRFABMS: *m*/*z* calcd forC₁₆H₂₇N₂, 247.2174; found, 247.2172.

Me₂NCMe₂CH=N(2,6-Me₂C₆H₃) (L2-1b). Me₂NCMe₂CHO (4.6 g, 0.04 mol) and 2,6-dimethylaniline (6.0 g, 0.05 mmol) were placed in 30 mL of toluene Formic acid (0.3 mL 99% v/v aqueous solution) was added, and the solution was refluxed in a set-up with Dean-Stark trap for 1 day. Toluene was removed under *vacuo*. The product was isolated by distillation to give a viscous yellow liquid in 58% yields (5.06 g). IR(KBr) $v_{C=N}$ 1662 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ 7.59 (s, 1H, CH=N), 7.01-6.86 (m, 3H, C₆H₃), 2.34 (s, 6H, NCH₃), 2.07 (s, 6H, (C₆H₃)CH₃), 1.31 (s, 6H, CCH₃); ¹³C NMR (CDCl₃, 100.625 MHz): δ 173.2 (CH=N), 150.5, 128-123 (phenyl-*C*), 61.5 (CCH₃), 39.2 (NCH₃), 20.0 (CCH₃), 18.4 ((C₆H₃)CH₃); HRFABMS: *m/z* calcd forC₁₄H₂₃N₂, 219.1861; found, 219.1862.

Me₂NCMe₂CH=N(2,6-ⁱPr₂C₆H₃) (L2-1d). Following the same procedure used for L2-1b, 4.6g (0.04 mol) of Me₂NCMe₂CHO and 8.8g (0.05 mol) of 2,6-diisoproylaniline were converted to a viscous yellow liquid of L2-1d; 6.03 g (47 %). IR(KBr) $v_{C=N}$ 1626 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.60 (s, 1H, CH=N), 7.10-7.01 (m, 3H, C₆H₃), 2.90 (h, $J_{H-H} = 6.9$ Hz, 2H, $CH(CH_3)_2$), 2.35 (s, 6H, NCH₃), 1.32 (s, 6H, CCH₃), 1.15 (d, $J_{H-H} = 6.9$ Hz, 12H, CH(CH₃)₂); ¹³C NMR (CDCl₃, 100.625 MHz): δ 170.3 (CH=N), 148.2-122.8 (phenyl-*C*), 61.8 (CCH₃), 39.2 (NCH₃), 27.6 (CH(CH₃)₂), 22.2 (CH(CH₃)₂), 20.0 (CCH₃); MS (FAB, m/z): 275.2 (M⁺+1); Anal. Calcd for C₁₈H₃₀N₂: C, 78.78; H, 11.02; N, 10.20. Found: C, 77.73; H, 11.19; N, 9.31.

Et₂**NCMe**₂**CH=NC**₆**H**₅ (**L2-2a**). Et₂NCMe₂CHO (11.4 g, 0.08 mol) and aniline (7.4 g, 0.08 mmol) were placed in 30 mL of toluene Formic acid (0.3 mL 99% v/v aqueous solution) was added, and the solution was refluxed in a set-up with Dean-Stark trap for 1 day. Toluene was removed under *vacuo*. The product was isolated by distillation to give a viscous yellow liquid in 66% yields (11.5 g). IR (KBr) $v_{C=N}$ 1648 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.76 (s, 1H, *HC*=N), 7.36-7.0 (m, 5H, C₆*H*₅), 2.70 (q, *J*_{H-H}= 7.1 Hz, 4H, NC*H*₂CH₃), 1.34 (s, 6H, CC*H*₃), 1.05 (t, *J*_{H-H} = 7.1 Hz, 6H, NCH₂C*H*₃); ¹³C NMR (CDCl₃, 75.469 MHz): δ 172.6 (*C*=N), 151.8, 130-112 (phenyl-*C*), 63.0 (*C*CH₃), 43.8 (*NC*H₂CH₃), 21.8 (*CC*H₃), 15.8 (NCH₂CH₃); MS (FAB, m/z): 219.2 (M⁺+1); Anal. Calcd for C₁₄H₂₂N₂: C, 77.01; H, 10.16; N, 12.83. Found: C, 76.43; H, 10.01; N, 12.32.

Et₂**NCMe**₂**CH=N(2,6-Me**₂**C**₆**H**₃) (**L2-2b**). Following the same procedure used for **L2-2a**, 10.0g (0.07 mol) of Et₂NCMe₂CHO and 8.5g (0.07 mol) of 2,6-dimethylaniline were converted to a viscous yellow liquid of **L2-2b**; 8.6 g (50%). IR(KBr) $v_{C=N}$ 1667 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.58 (s, 1H, CH=N), 7.01-6.88 (m, 3H, C₆H₃), 2.66 (q, J_{H-H} = 7.1 Hz, 4H, NCH₂CH₃), 2.07 (s, 6H, (C₆H₃)CH₃), 1.34 (s, 6H, CCH₃), 1.06 (t, J_{H-H} = 7.1 Hz, 6H, NCH₂CH₃); ¹³C NMR (CDCl₃, 75.469 MHz): δ 174.3 (CH=N), 150.5, 128-123 (phenyl-*C*), 63.0 (CCH₃), 43.7 (NCH₂CH₃), 22.1 (CCH₃), 18.3 ((C₆H₃)CH₃), 16.5 (NCH₂CH₃); HRFABMS: *m*/*z* calcd forC₁₆H₂₇N₂, 247.2174; found, 247.2175; Anal. Calcd for C₁₆H₂₆N₂: C, 78.00; H, 10.64; N, 11.37. Found: C, 77.64; H, 10.45; N, 11.39.

Et₂**NCMe**₂**CH=N(2,6-Et**₂**C**₆**H**₃) (**L2-2c**). Following the same procedure used for **L2-2a**, 10.0g (0.07 mol) of Et₂NCMe₂CHO and 10.4g (0.07 mol) of 2,6-diethylaniline were converted to a viscous yellow liquid of **L2-2c**; 8.8 g (46%). IR(KBr) $v_{C=N}$ 1664 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.60 (s, 1H, C*H*=N), 7.03-6.97 (m, 3H, C₆*H*₃), 2.67 (q, *J*_{H-H} = 7.1 Hz, 4H, NC*H*₂CH₃), 2.07 (q, *J*_{H-H} = 7.4 Hz, 4H, (C₆H₃)C*H*₂CH₃), 1.34 (s, 6H, CC*H*₃), 1.12 (t, *J*_{H-H} = 7.4 Hz, 6H, (C₆H₃)CH₂C*H*₃), 1.07 (t, *J*_{H-H} = 7.1 Hz, 6H, NCH₂C*H*₃); ¹³C NMR (CDCl₃, 75.469 MHz): δ 173.4 (*C*H=N), 149.5, 132-123 (phenyl-*C*), 63.0 (*C*CH₃), 43.7 (NCH₂CH₃), 29.6 ((C₆H₃) *C*H₂CH₃), 24.5 ((C₆H₃) CH₂CH₃), 22.0 (CCH₃), 16.5 (NCH₂CH₃); HRFABMS: *m/z* calcd for C₁₈H₃₁N₂, 275.2487; found, 275.2489. Anal. Calcd for C₁₈H₃₀N₂: C, 78.77; H, 11.02; N, 10.21. Found: C, 77.92; H, 10.57; N, 9.53.

Et₂NCMe₂CH=N(2,6-ⁱPr₂C₆H₃) (L2-2d). Following the same procedure used for L2-2a, 10.0g (0.07 mol) of Et₂NCMe₂CHO and 12.4g (0.07 mol) of 2,6-diisoproylaniline were converted to a viscous yellow liquid of L2-2d; 9.3 g (44%). IR(KBr) $v_{C=N}$ 1666 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.56 (s, 1H, CH=N), 7.09-7.05 (m, 3H, C₆H₃), 2.88 (h, $J_{H-H} =$ 7.1 Hz, 2H, CH(CH₃)₂) 2.65 (q, $J_{H-H} =$ 7.1 Hz, 4H, NCH₂CH₃), 1.33 (s, 6H, CCH₃), 1.13 (d, $J_{H-H} =$ 7.1 Hz, 12H, CH(CH₃)₂), 1.05 (t, $J_{H-H} =$ 7.1 Hz, 6H, NCH₂CH₃); ¹³C NMR (CDCl₃, 75.469 MHz): δ 173.7 (CH=N), 148.3, 137.4, 123.7, 122.8 (phenyl-C), 63.2 (CCH₃), 43.8 (NCH₂CH₃), 29.7(CH(CH₃)₂), 27.6(NCH₂CH₃), 23.5 (CH(CH₃)₂), 22.2 (CCH₃), 16.5 (NCH₂CH₃); MS (FAB, m/z): 275.2 (M⁺+1). Anal. Calcd for C₂₀H₃₄N₂: C, 79.41; H, 11.32; N, 9.26. Found: C, 79.70; H, 11.62; N, 9.15.

ⁿPr₂NC(Me)₂CH=N(2,6-ⁱPr₂C₆H₃) (L2-3d). ⁿPr₂NCMe₂CHO (3.42 g, 0.02 mol) and 2,6-diisopropylaniline (3.55 g, 0.02 mol) were placed in 30 mL of toluene. Formic acid (0.3 mL 99% v/v aqueous solution) was added, and the solution was refluxed in a set-up with

Dean-Stark trap for 1 day. Toluene was removed under *vacuo*. The product was isolated by distillation to give a viscous yellow liquid in 40 % yields (2.74 g). IR(KBr) $v_{C=N}$ 1666 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 7.59 (s, 1H, CH=N), 7.12-7.04 (m, 3H, C₆H₃), 2.90 (h, $J_{H-H} = 6.7$ Hz, 2H, CH(CH₃)₂), 2.51 (m, 4H, CH₂CH₂CH₃), 1.47 (m, $J_{H-H} = 7.2$ Hz, 4H, NCH₂CH₂CH₃), 1.33 (s, 6H, CCH₃), 1.60 (d, $J_{H-H} = 6.7$ Hz, 12H, CH(CH₃)₂) 0.85 (t, $J_{H-H} = 7.2$ Hz, 6H, NCH₂CH₂CH₃); ¹³C NMR (CDCl₃, 75.469 MHz): δ 173.8 (CH=N), 148.3, 137.4, 123.7, 122.8 (phenyl-C), 63.1 (CCH₃), 53.3 (NCH₂CH₂CH₃), 27.5 (CH(CH₃)₂), 24.5 (NCH₂CH₂CH₃), 23.5 (CH(CH₃)₂), 22.1 (CCH₃), 11.7 (NCH₂CH₂CH₃); MS (FAB, m/z): 329.3 (M⁺+1); Anal. Calcd for C₂₂H₃₈N₂: C, 79.95; H, 11.59; N, 8.47. Found: C, 79.40; H, 11.60; N, 8.24.

c-C₄H₈NCMe₂CH=N(2,6⁻ⁱPr₂C₆H₃) (L2-4d). c-C₄H₈NCMe₂CHO (10.0 g, 0.07 mol) and 2,6-diisopropylaniline (14.1 g, 0.08 mol) were placed in 30 mL of toluene Formic acid (0.3 mL 99% v/v aqueous solution) was added, and the solution was refluxed in a set-up with Dean-Stark trap for 1 day. Toluene was removed under *vacuo*. The product was isolated by crystallization to give a yellow solid in 50% yields (10.5 g). IR(KBr) v_{C=N} 1666 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): ¹H NMR (CDCl₃, 300 MHz): δ 7.67 (s, 1H, CH=N), 7.10-7.01 (m, 3H, C₆H₃), 2.89 (h, *J*_{H-H} = 7.1 Hz, 2H, CH(CH₃)₂) 2.78 (m, 4H, NCH₂CH₃), 1.77 (m, 4H, NCH₂CH₂), 1.38 (s, 6H, CCH₃), 1.13 (d, *J*_{H-H} = 7.1 Hz, 12H, CH(CH₃)₂); ¹³C NMR (CDCl₃, 75.469 MHz): δ 172.1 (CH=N), 148.5, 137.4~122.8 (phenyl-C), 59.7 (CCH₃), 46.5 (NCH₂CH₃), 27.6 (CH(CH₃)₂), 24.1 (NCH₂CH₃), 23.5 (CH(CH₃)₂), 21.8 (CCH₃); MS (FAB, m/z): 301.2 (M⁺+1); Anal. Calcd for C₂₀H₃₂N₂: C, 79.94; H, 10.73; N, 9.32. Found: C, 80.32; H, 11.12; N, 9.27.

[Me₂NCH₂CH=N(2,6-ⁱPr₂C₆H₃)]NiBr₂ (Ni1-1d). (DME)NiBr₂ (324mg, 1.05 mmol) and L1-1d (340 mg, 1.38 mmol) were placed in a round-bottom flask under nitrogen. Predried CH₂Cl₂ (15 mL) was transferred under vacuo. The reaction was stirred at room temperature for 6 h. The supernatant liquid was removed, and the product was dried in vacuo. The product Ni1-1d was isolated as an orange-brown powder (385 mg, 79% yield). HRFABMS: m/z calcd for C₁₆H₂₆N₂NiBr, 383.0633; found, 383.0624.

[Me₂NCMe₂C=N(2,6-Me₂C₆H₃)]NiBr₂ (Ni2-1b). (DME)NiBr₂ (300mg, 1 mmol) and L2-1b (327 mg, 1.5 mmol) were placed in a round-bottom flask under nitrogen. Predried CH₂Cl₂(15 mL) was transferred under vacuo. The orange solution turned to violet within 10 minutes. The reaction was allowed to complete at 25 °C. After removal of the

supernatant solid, the reaction solution was concentrated. Addition of dry Et₂O resulted in the solid product, and the yield of **Ni2-1b** was 74% (321 mg) after recrystallization from CH₂Cl₂/Et₂O. MS (FAB, m/z): 355.0 (M^+ -Br); Anal. Calcd for C₁₄H₂₂N₂Br₂Ni: C, 38.49; H, 5.08; N, 6.41. Found: C, 38.57; H, 5.06; N, 6.04; Crystals suitable for an X-ray diffraction experiment were obtained by slow diffusion of ether into a saturated dichloromethane solution of **Ni2-1b**.

[Me₂NCMe₂C=N(2,6-ⁱPr₂C₆H₃)]NiBr₂ (Ni2-1d). Following the same procedure used for Ni2-1b, the reaction of (DME)NiBr₂ (100mg, 1 mmol) and L2-2a (130mg, 0.49 mmol) gave violet solid of Ni2-1d (92mg, yield: 57%). MS (FAB, m/z): 411.1 (M⁺-Br); Anal. Calcd for C₁₈H₃₀N₂Br₂Ni: C, 43.86; H, 6.13; N, 5.68. Found: C, 43.68; H, 6.12; N, 5.34; Crystals suitable for an X-ray diffraction experiment were obtained by slow diffusion of ether into a saturated dichloromethane solution of Ni2-1d.

[Et₂NCMe₂CH=NC₆H₅]NiBr₂ (Ni2-2a). Following the same procedure used for Ni2-1b, the reaction of (DME)NiBr₂ (300mg, 1 mmol) and L2-2a (327mg, 1.5 mmol) gave violet solid of Ni2-2a (264mg, yield: 62%). ¹H NMR (CDCl₃, 300 MHz): δ 8.56 (s, 1H, CH=N), 7.44-7.18 (m, 5H, phenyl-*H*), 3.37, 2.96 (m, m, 2H, 2H, NCH₂CH₃), 1.74 (s, 6H, CCH₃), 1.59 (t, *J*_{H-H} = 7.1 Hz, 6H, NCH₂CH₃); ¹³C NMR (CDCl₃, 75.469 MHz): δ 161.1 (CH=N), 148.4, 128.8, 126.9, 120.8 (phenyl-*C*), 69.0 (CCH₃), 46.2 (NCH₂CH₃), 21.2 (CCH₃), 11.8 (NCH₂CH₃). MS (FAB, m/z): 355.0 (M⁺-Br). Anal. Calcd for C₁₄H₂₂Br₂N₂Ni : C, 38.49; H, 5.08; N, 6.41. Found: C, 38.78; H, 5.03; N, 6.37; Crystals suitable for an X-ray diffraction experiment were obtained by slow diffusion of ether into a saturated dichloromethane solution of Ni2-2a.

[Et₂NCMe₂C=N(2,6-Me₂C₆H₃)]NiBr₂ (Ni2-2b). Following the same procedure used for Ni2-1b, the reaction of (DME)NiBr₂ (300mg, 1 mmol) and L2-2b (358 mg, 1.5 mmol) gave violet solid of Ni2-2b (264mg, yield: 57%). ¹H NMR (CDCl₃, 300 MHz): δ 8.29 (s, 1H, CH=N), 7.06-6.98 (m, 3H, phenyl-H), 3.45, 3.07 (m, m J_{H-H} = 7.1 Hz, 2H, 2H, NCH₂CH₃), 2.10 (s, 6H, (C₆H₃)CH₃), 1.83 (s, 6H, CCH₃), 1.70 (t, J_{H-H} = 7.1 Hz, 6H, NCH₂CH₃); ¹³C NMR (CDCl₃, 75.469 MHz): δ 164.4 (CH=N), 147.9, 127.9, 125.6, 124.1, (phenyl-C), 69.8 (CCH₃), 46.6 (NCH₂CH₃), 21.4 (CCH₃), 18.3 ((C₆H₃)CH₃), 11.9 (NCH₂CH₃); MS (FAB, m/z): 383.1 (M⁺-Br); Anal. Calcd for C₁₆H₂₆Br₂N₂Ni·0.324 CH₂Cl₂: C, 45.92; H, 6.41; N, 6.03. Found: C, 45.92; H, 6.40; N, 6.48; Crystals suitable for an X-ray diffraction experiment were obtained by slow diffusion of ether into a saturated dichloromethane solution of Ni2-2b. [Et₂NCMe₂C=N(2,6-ⁱPr₂C₆H₃)]NiBr₂ (Ni2-2d). Following the same procedure used for Ni2-1b, the reaction of (DME)NiBr₂ (300mg, 1 mmol) and L2-2d (453 mg, 1.5 mmol) gave violet solid of Ni2-2d (291mg, yield: 56%). ¹H NMR (CDCl₃, 300 MHz): δ 8.29 (s, 1H, CH=N), 7.14 (br, 3H, phenyl-H), 3.49, 3.12 (br, 2H, 2H, NCH₂CH₃), 2.73 (br, 1H, CH(CH₃)₂)), 1.85 (s, 6H, CCH₃), 1.74 (br, 6H, NCH₂CH₃), 1.19 (br, 6H, CH(CH₃)₂)); ¹³C NMR (CDCl₃, 75.469 MHz): δ 163.9 (CH=N), 150.3, 136.0, 124.5 122.5 (phenyl-C), 70.0 (CCH₃), 46.6 (NCH₂CH₃), 27.5 (CH(CH₃)₂), 23.1 (CH(CH₃)₂), 21.4 CH(CH₃)₂), 12.0 (NCH₂CH₃); MS (FAB, m/z): 439.1 (M⁺-Br); Anal. Calcd for C₂₀H₃₄N₂Br₂Ni: C, 46.11; H, 6.58; N, 5.38. Found: C, 46.33; H, 6.47; N, 5.11.

 $[^{n}Pr_{2}NCMe_{2}C=N(2,6^{-i}Pr_{2}C_{6}H_{3})]NiBr_{2}$ (Ni2-3d). Following the same procedure used for Ni2-1b, the reaction of (DME)NiBr₂ (100mg, 0.32 mmol) and L2-3a (160 mg, 0.49 mmol) gave violet solid of Ni2-3d (72mg, yield: 40%). MS (FAB, m/z): 413 (M⁺-Br). Anal. Calcd for C₂₂H₃₈N₂Br₂Ni: C, 48.13; H, 6.98; N, 5.10. Found: C, 48.78; H, 7.51; N, 4.71.

[c-C₄H₈NCMe₂C=N(2,6-ⁱPr₂C₆H₃)]NiBr₂ (Ni2-4d). Following the same procedure used for Ni2-1b, the reaction of (DME)NiBr₂ (100mg, 0.32 mmol) and L2-4d (150 mg, 0.49 mmol) gave violet solid of Ni2-4d (52mg, yield: 53%). MS (FAB, m/z): 413 (M⁺-Br). Anal. Calcd for C₂₀H₃₂N₂NiBr₂: C, 46.29; H, 6.21; N, 5.40. Found: C, 45.93; H, 6.12; N, 5.20.

General Procedure for High-Pressure Polymerization of Ethylene

Into a 600 mL Parr autoclave was placed Ni (N-N') Br_2 (10-12 mg) and MAO (6 mL) in dried toluene. Then the autoclave was sealed. Upon flash with ethylene gas several times, ethylene gas was pressurized. During the reaction, ethylene was refilled when the pressure was found to drop. The mixture was stirred for a period of time. The reaction was quenched with venting the autoclave followed by addition of methanol/HCl (4:1). The precipitated polymers were filtered from solution and dried in vacuo.

In a typical run, to a 600 mL autoclave was placed 22 μ mol of the catalyst and 6 mL MAO in 100 mL predried toluene. The autoclave was sealed and flushed with ethylene several times. Ethylene then was pressurized to 250 psi that was maintained and the reaction ran at 25 °C for 3h. The reaction was quenched by venting the autoclave. To the solution, was added methanol/HCl in 4:1 v/v ratio. Toluene was used to extract the organic, and methanol or acetone was to precipitate the PE. The GPC analysis was done to the soluble

part in toluene solutions. The high temperature GPC analysis was done to a sample dissolving in $1,3,5-C_6H_3Cl_3$ to 130 °C.

General Procedure for Polymerizations of Norbornene

To a 100 mL round-bottom flask was placed Ni(N-N')Br₂. and MAO in dried toluene. Norbornene was added, and then the flask was sealed with septum. The mixture was stirred for a period of time. The reaction was quenched with addition of methanol/HCl (4:1). The precipitated polymers were filtered from solution and dried in vacuo.

X-ray Crystallographic Analysis

Diffraction data were measured on a Nonius CAD-4 diffractometer with graphite-monochromatized Mo K_{α} radiation. The cell parameters were determined by a least-squares fit on 25 reflections. Intensity data were corrected for absorption on the basis of an experimental ψ rotation curve. The refinement procedure was by a full-matrix least-squares method including all the non-hydrogenic atoms anisotropically. Hydrogen atoms were fixed at the ideal geometry and the C-H distance of 1.0 _; their isotopic thermal parameters were fixed to the values of the attached carbon atoms at the convergence of the isotropic refinement. Atomic scattering factors were taken from the International Tables of Crystallographic Data, Vol IV [15]. Computing programs are from the NRC VAX package [16]. Crystallographic data and selected atomic coordinates and bond parameters are collected in Tables III-IX. The rest of data are supplied in the supplementary material.