

Novel Nickel Catalysts Containing Tetradentate Chelating Ligands for the Polymerization of Norbornene

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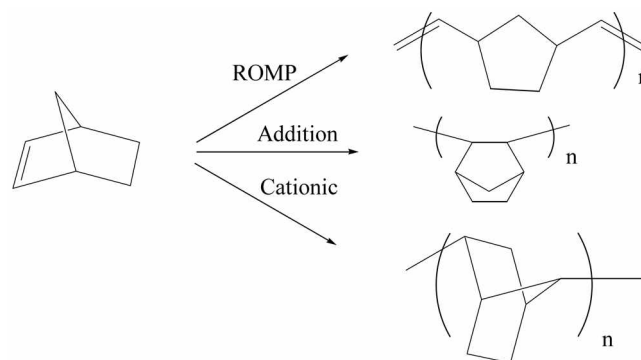
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New nickel complexes containing novel tetradentate ligands, 4,5-substituted-1,2-bis(pyridine-2-carboxamide)-benzene ligands but lacking alkyl or halide ligands in the coordination sphere have been prepared. They were activated with MMAO (modified methylaluminoxane) to be proven as efficient catalysts for the polymerization of norbornene. Both electron-donating and -withdrawing substituents on the benzene ring and polar solvents enhance the catalytic activity for olefin polymerization. Improvement in thermal stability of the complexes was observed. Some of these complexes were crystallographically determined to have square planar geometry. A plausible mechanism involving dissociation of ligands is proposed.

Key Words : Nickel complexes, Tetradentate ligands, 4,5-Substituted-1,2-bis(pyridine-2-carboxamide)-benzene, MMAO, Norbornene polymerization

Introduction

Polynorbornenes have drawn much interest due to their unique physical properties such as high glass transition temperature, optical transparency, low dielectric properties and birefringence, which can be applicable in the new optical information storage media, microelectronics, packing and gas separation.¹⁻⁴ In these polymers, retention of bicyclic structure of the monomer units and strict restriction of rotation between the neighboring bulky units are the reasons for their unique properties. Norbornene is known to be polymerized by ring-opening metathesis polymerization (ROMP), cationic polymerization and vinyl addition polymerization (Scheme 1). Since the first adoption of a $\text{TiCl}_4/\text{Al}^i\text{Bu}_3$ catalyst in the early 1960s, various catalysts from Ni, Co, Cr, Ti, Zr and Pd complexes have been used for norbornene vinyl polymerization.⁵ Generally, early transition metal complexes such as zirconocenes have shown lower activities than late transition metal ones. However, much improved systems based on early transition metal have been continuously reported⁶ and $(t\text{-BuNSiMe}_2\text{Flu})\text{TiMe}_2$ with various cocatalysts showed living nature in the norbornene polymerization.⁷ Even though crystalline polymers have been reported,⁸ most polynorbornenes by addition polymerization are amorphous and the structures are assumed to have a rigid random coil conformation.^{9,10} The processibility, brittleness and adhesion properties of unsubstituted polynorbornenes have prevented the further applications. Therefore, current research has been focused on the vinyl addition polymerization of norbornene derivatives with pendant functionalities and ethylene and/or 1-alkene/norbornene copolymerization to improve these properties.^{11,12} Commercial production of cyclic olefins copolymers (COCs) in the names of APEL and TOPAS by Mitsui and Ticona (formerly Hoechst),



Scheme 1. Polymerization Mechanisms for Norbornene.

respectively, represents the development in this field.

Since late transition metals have been known to tolerate oxygen functionalities in the monomer and the polymer much more than early transition metals, recent research activities have been focused on the development of late transition metal catalysts with enhanced performance.¹³ Reported catalytic systems are mainly based on Ni and Pd complexes containing various bidentate $\text{P}^{\wedge}\text{O}$, $\text{N}^{\wedge}\text{O}$, $\text{P}^{\wedge}\text{P}$ and $\text{N}^{\wedge}\text{N}$ ligands with bulky aryl substituents. Late transition metal complexes with tri or higher dentate ligands are generally known to be inactive or less active for olefin polymerizations than ones with bidentate ligands.¹⁴ However, some nickel complexes with functionalized bipyridine ligands, potentially tetradentate ligands, have been recently reported to show high catalytic activity toward norbornene polymerization.¹⁵

Herein we report another Ni system containing rigid and tetradentate ligands, which are highly active towards norbornene polymerization.

Experimental Section

All the works involving moisture-sensitive compounds were carried out using standard Schlenk or dry-box techniques. ^1H NMR spectra were recorded on Oxford Unity 300 spectrometer at ambient temperature. IR spectra were measured on a BIO RAD FTS 135 spectrometer as KBr pellets. Elemental analyses were performed with EA-1110 (CE Instruments) in the Inha University. Molecular weight measurements were made on a GPC system (Waters 150C) equipped with a refractive index detector in Samsung Atofina Co. Polymer samples were dissolved in chlorobenzene (50 mg/15 mL) and filtered through a 0.45 Teflon filter. All molecular weights are relative to polystyrene standards.

Preparation of ligands. For the preparation of the ligand 4-fluoro-1,2-bis(2-pyridine-2-carboxamino) benzene (H_2bpf : **2**), a modification of the method of Lee *et al.*^{16c} was used. To a stirred solution of picolinic acid (0.147 g, 1.2 mmol) in pyridine (4 mL), a solution of 4-fluoro-*o*-1,2-phenylenediamine (0.076 g, 0.6 mmol) in pyridine (1 mL) was added dropwise. The solution was stirred for 15 min and triphenyl phosphite (0.32 mL, 1.2 mmol) was slowly added. The temperature of the reaction mixture was increased to 100 °C, and the mixture was stirred for 2 h. The volume was then reduced to 2 mL and kept in air. Crystallization from ethanol and water afforded white powder and washed with ethanol.

^1H NMR (CDCl_3 , 300 MHz): δ 6.95-8.64 (m, 11H, aromatic-H), 10.03 (s, 1H, N-H), 10.42 (s, 1H, N-H). IR (KBr): ν (N-H) 3319 and 3272 and ν (C=O) 1695 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{13}\text{FN}_4\text{O}_2$: C, 64.28; H, 3.90; N, 16.66. Found: C, 64.23; H, 3.95; N, 16.77. Ligands **1** (H_2bpn) and **7** (H_2MeObpb) were synthesized by the same method as the above. For **1**, ^1H NMR (CDCl_3 , 300 MHz): δ 6.80-8.80 (m, 11H, aromatic-H), 10.20 (s, 1H, N-H), 11.10 (s, 1H, N-H). IR (KBr): ν (N-H) 3337 and 3270 and ν (C=O) 1703 and 1668 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{13}\text{N}_5\text{O}_4$: C, 59.50; H, 3.61; N, 19.28. Found: C, 59.53; H, 3.55; N, 19.01. For **7**, ^1H NMR (CDCl_3 , 300 MHz): δ 3.90 (s, 3H, CH_3), 6.75-8.65 (m, 11H, aromatic-H), 9.93 (s, 1H, N-H), 10.40 (s, 1H, N-H). IR (KBr): ν (N-H) 3328 and 3279 and ν (C=O) 1696 cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{16}\text{N}_4\text{O}_3$: C, 65.51; H, 4.63; N, 16.08. Found: C, 65.44; H, 4.79; N, 16.11.

Preparation of complexes. The complexes **8-14** have been prepared by the same method to the synthesis of **11**.¹⁷ For **8**, IR (KBr): ν (C=O) 1657 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{11}\text{N}_5\text{NiO}_4$: C, 51.47; H, 2.64; N, 16.67. Found: C, 50.95; H, 2.61; N, 16.74. For **9**, ^1H NMR (DMSO, 300 MHz): δ 6.55-8.60 (m, 11H, aromatic-H). IR (KBr): ν (C=O) 1644 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{11}\text{FN}_4\text{NiO}_2$: C, 55.01; H, 2.82; N, 14.26. Found: C, 55.49; H, 2.66; N, 14.10. For **10**, IR (KBr): ν (C=O) 1650 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{10}\text{Cl}_2\text{N}_4\text{NiO}_2$: C, 48.70; H, 2.27; N, 12.62. Found: C, 48.73; H, 2.24; N, 12.60. For **12**, ^1H NMR (DMSO, 300 MHz): δ 2.18 (s, 3H, CH_3), 6.54-8.43 (m, 11H, aromatic-H). IR (KBr): ν (C=O) 1644 cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{N}_4\text{NiO}_2$: C, 58.66; H, 3.63; N, 14.40. Found: C, 58.29; H, 3.40; N, 14.72. For **13**, ^1H NMR (DMSO, 300 MHz): δ 2.20 (s, 6H,

2 CH_3), 7.51-8.46 (m, 10H, aromatic-H). IR (KBr): ν (C=O) 1644 cm^{-1} . Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{N}_4\text{NiO}_2$: C, 59.60; H, 4.00; N, 13.90. Found: C, 59.54; H, 4.26; N, 13.91. For **14**, ^1H NMR (DMSO, 300 MHz): δ 3.67 (s, 3H, CH_3), 6.36-8.48 (m, 11H, aromatic-H). IR (KBr): ν (C=O) 1640 cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{N}_4\text{NiO}_3$: C, 56.34; H, 3.48; N, 13.83. Found: C, 56.19; H, 3.74; N, 13.48.

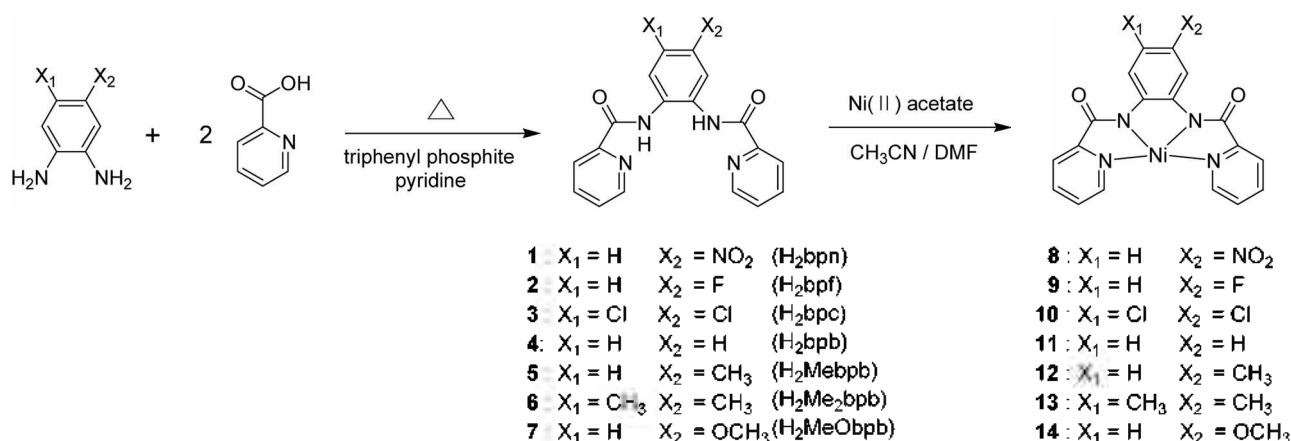
X-ray crystallography. The diffraction data for compounds $[\text{Ni}(\text{bpf})]$ **9**, $[\text{Ni}(\text{bpc})]$ **10**, and $[\text{Ni}(\text{Me}_2\text{bpb})]$ **13** were collected on a Nonius Kappa-CCD diffractometer using $\text{Mo K}\alpha$ ($\lambda = 0.71073$ Å). The crystals were mounted on glass fibers under epoxy. The CCD data were integrated and scaled using a DENZO-SMN software package, and the structures were solved and refined using SHEXTL V5.0. Hydrogen atoms were located in the calculated positions.

The quality of crystal of **12** was not very good, but data was collected successfully. The structure was solved with a little high R value. The diffraction data for compound **12** were collected on a Bruker SMART diffractometer using $\text{Mo K}\alpha$ ($\lambda = 0.71073$ Å). The crystals were mounted on glass fibers under epoxy. The CCD data were integrated and scaled using a Bruker SAINT, and the structures were solved and refined using Bruker SHELXTL. Hydrogen atoms were located in the calculated positions. The molecular structure was drawn by the Ortep-3 for Windows program. The crystallographic data for compounds **9**, **10**, **12**, and **13** are listed in Table 1.

Polymerization condition. In an inert (N_2) atmosphere, MMAO (catalyst : cocatalyst = 1 : 1000 eq) was placed into a small vial. To this, approximately 10 mL of solvent was added and the mixture was gently stirred to dissolve the solids. This solution was then transferred to a 20 mL-vial with a stirring bar containing 2.4×10^{-2} mmol of catalyst, 1000 equivalent of norbornene and 10 mL of solvent. The solution was stirred rapidly for about 10 minutes. The reaction was quenched with acidic methanol (methanol/conc. $\text{HCl} = 50/1$) and the solid was filtered and dried under vacuum at 100 °C for 12 h.

Results and Discussion

Syntheses. Ligands **1-7** were prepared in good yields (60-80%) by the reactions between appropriate diamines with 2-picolinic acid in pyridine in the presence of triphenylphosphite (Scheme 1) according to the literature method¹⁶ or its modified method described in the experimental section. The complexes **8-14** were obtained from the reaction of each ligand with nickel(II) acetate dihydrate in $\text{CH}_3\text{CN}/\text{DMF}$ (15/5) in excellent yields. The complex **11** was reddish-yellow as previously reported in the literature¹⁷ and the rest complexes were isolated as brownish-yellow solid for **9** and **10**, orange ones for **8** and **13**, and yellowish-orange ones for **12** and **14**, which are sparingly soluble in most common organic solvents, except DMSO and DMF. Crystals of the complexes **9**, **10**, **12** and **13** were grown by slowly evaporating their solutions in pyridine/ether. All complexes are stable in the air.



Scheme 2. Syntheses of ligands and their Ni complexes.

Structures of the complexes. The structures of [Ni(bpf)] **9**, [Ni(bpc)] **10** and [Ni(Me**bpb**)] **13** are shown in Figure 1. These structures are nearly similar to that of compound **11**¹⁷ with a planar molecular arrangement. Four N atoms of the bp²⁻ ligand (H₂bpf = 4-fluoro-1,2-bis(pyridine-2-carboxamide)benzene) and four N atoms of the bpc²⁻ ligand (H₂bpc = 4,5-dichloro-1,2-bis(pyridine-2-carboxamide)benzene) are coordinated to the Ni(II) atoms in each compound **9** and **10**, respectively. The inner Ni-N distances of both compounds **9** and **10** of about 1.84 Å are somewhat shorter than the outer

Ni-N distances of both compounds **9** and **10** of about 1.94 Å (see Table 2). The inner Ni-N distance of **13** of 1.920(2) Å are also somewhat shorter than the outer Ni-N distance of 2.020(2) Å. The coordination geometry of Ni atom in those compounds is nearly square planar. The F atom in compound **9** is disordered over two positions (C9 and C10). The pyridine rings are a little tilted from the N1/N2/N3/N4 plane with torsion angles C18-N4-Ni1-N1 of 9.04(2)° for compound **9**, C5-N1-Ni1-N1 of 7.98(2)° for compound **10**, and C1-N1-Ni1-N1 of -5.94(2)° for compound **13**. The com-

Table 1. Crystallographic data for compounds **9**, **10**, **12**, and **13**

	Ni(bpf) 9	Ni(bpc) 10	Ni(Me bpb) 12 ^a	Ni(Me ₂ bpb) 13
Empirical formula	C ₁₈ H ₁₁ F N ₄ Ni O ₂	C ₁₈ H ₁₀ Cl ₂ N ₄ Ni O ₂	C ₁₉ H ₁₄ N ₄ Ni O ₂	C ₂₀ H ₁₆ N ₄ Ni O ₂
Formula weight	393.02	443.91	389.01	403.08
Temperature	150(1) K	150(1) K	273(2) K	150(1)
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Space group	P 2 ₁ /c	Pbcn	Cmc2 ₁	Pbcn
a	10.4189(9) Å	18.2227(3) Å	18.859(5) Å	18.3109(2)
b	20.162(2) Å	13.1172(6) Å	12.671(3) Å	13.1003(4)
c	7.3486(6) Å	6.8571(9) Å	6.961(2) Å	6.8599(7)
α	90°	90°	90°	90°
β	100.008(4)°	90°	90°	90°
γ	90°	90°	90°	90°
Volume	1285.7(5) Å ³	1639.1(2) Å ³	1663.4(8) Å ³	1645.54(18)
Z	4	4	4	4
Density (calc.)	1.717 Mg/m ³	1.799 Mg/m ³	1.549 Mg/m ³	1.627 Mg/m ³
Absorption coeff.	1.310 mm ⁻¹	1.533 mm ⁻¹	1.188 mm ⁻¹	1.204 mm ⁻¹
F(000)	800	896	796	832
Crystal size	0.20 × 0.04 × 0.04 mm ³	0.17 × 0.04 × 0.03 mm ³	0.20 × 0.05 × 0.05 mm ³	0.20 × 0.08 × 0.04 mm ³
Reflections collected	12137	9284	4999	8635
Independent reflections	3492 [R(int)=0.163]	1880 [R(int)=0.0738]	1917 [R(int)=0.0704]	1891 [R(int)=0.0546]
Data / restraints / parameters	3492 / 1 / 241	1880 / 0 / 124	1917 / 20 / 127	1891 / 0 / 125
Goodness-of-fit on F ²	0.966	1.035	1.047	1.071
Final R indices [I > 2σ(I)]	R ₁ = 0.0652, wR ₂ = 0.1317	R ₁ = 0.0441, wR ₂ = 0.0983	R ₁ = 0.0984, wR ₂ = 0.2466	R ₁ = 0.0357, wR ₂ = 0.0779
R indices (all data)	R ₁ = 0.1645, wR ₂ = 0.1710	R ₁ = 0.0716, wR ₂ = 0.1117	R ₁ = 0.1786, wR ₂ = 0.3058	R ₁ = 0.0548, wR ₂ = 0.0852
Ext. coefficient	none	0.0038(11)	none	0.0050(10)
Largest diff. peak and hole	0.428 and -0.549 e.Å ⁻³	0.658 and -0.518 e.Å ⁻³	0.997 and -0.503 e.Å ⁻³	0.449 and -0.384 e.Å ⁻³

^aThe R value is a little high since the pyridyl ring is highly disordered and refined isotropically.

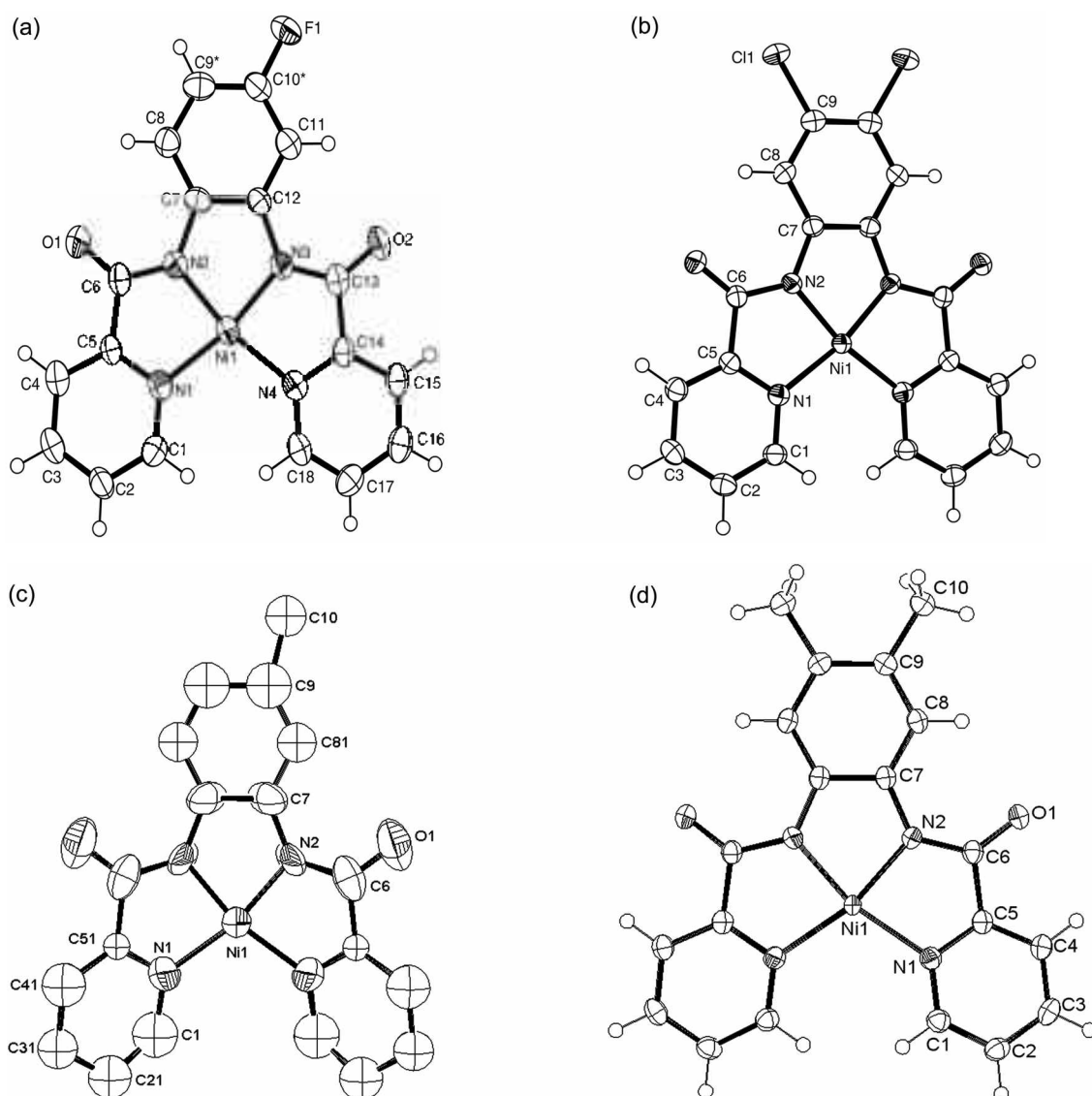


Figure 1. (a) The structure of [Ni(bpf)] **9**. The disordered F atom is not shown for clarity. (b) The structure of [Ni(bpc)] **10**. There is a mirror plane through the center of the molecule. Symmetry operation #1: $-x+1, y, -z+1/2$. (c) The structure of [Ni(Me₂bpb)] **12**. The disordered pyridyl ring and all hydrogen atoms were omitted for clarity. Symmetry operation #1: $-x+1, y, z$, #2: $-x+1, -y+2, z+1/2$, #3: $-x+1, -y+2, z-1/2$. (d) The structure of [Ni(Me₂bpb)] **13**. Symmetry operation #1: $-x+2, y, z$. There is a mirror plane through the center of the molecule. Symmetry operation #1: $-x+1, y, -z+1/2$.

Table 2. Selected bond lengths [Å] and angles [°] for compounds **9**, **10**, **12**, and **13**

	9	10	12	13
Inner Ni-N	1.942(5), 1.943(5) Å	1.949(2) Å	1.901(9) Å	2.020(2) Å
Outer Ni-N	1.834(5), 1.839(4) Å	1.846(2) Å	1.789(8) Å	1.920(2) Å
N(py)-Ni-N(py)	108.4(2)°	108.25(14)°	108.2(6)°	111.72(10)°
N-Ni-N (<i>cis</i>)	83.6(2)-84.5(2)°	83.9(1)-83.98(15)°	80.8(7)-85.5(4)°	82.75(7)-82.96(10)°
N-Ni-N (<i>trans</i>)	167.4(2), 167.8(2)°	167.7(1)°	166.1(4)°	165.28(7)°

pound [Ni(Me₂bpb)] **12** also shows a similar but rather distorted structure with a little higher R value and the pyridine rings are a lot more tilted from the N1/N2/N3/N4 plane with torsion angles C1-N1-Ni1-N1 of $-24(3)^\circ$ (see Figure 1 and Table 2).

Polymerization. Even though no terminal alkyl or halide

ligands are present, these complexes are surprisingly quite active towards norbornene polymerization in the presence of MAO. Polymerization results are summarized in Table 3. Polynorbornene was found to be amorphous and T_g cannot be determined from DSC experiments. PDI results in norbornene polymerization (Table 3) clearly show that these

Table 3. Polymerization of Norbornene by New Nickel Complexes

Catalysts	Solvent	T (°C)	Yield (g)	Activity (kg/Ni·mol·h)	M _w (× 10 ⁵)	PDI (M _w /M _n)
8	PhMe	25	0.30	845	6.18	1.99
		50	0.55	1549	5.89	2.20
9	PhMe	25	0.60	1703	13.8	2.44
		25	0.39	1106	5.73	2.18
10	PhMe	25	0.85	2160	11.20	2.83
		25	0.24	701	2.99	1.93
11	PhMe	25	0.31	854	8.14	2.19
		25	0.10	214	1.89	1.99
12	PhMe	25	0.26	736	4.21	2.11
		25	0.23	659	4.82	2.03
13	PhMe	25	0.28	805	10.03	2.32
		25	0.35	993	3.36	2.01
14	PhMe	50	0.46	1304	1.70	1.97
		70	0.62	1758	1.18	1.99
		100	0.53	1315	0.73	1.95
		25	0.36	1018	9.66	1.95
		50	1.20	1697	7.19	2.17
		70	1.53	2164	3.94	2.79
14	PhCl	25	0.49	1390	8.67	1.81
		25	0.59	1673	9.46	1.98

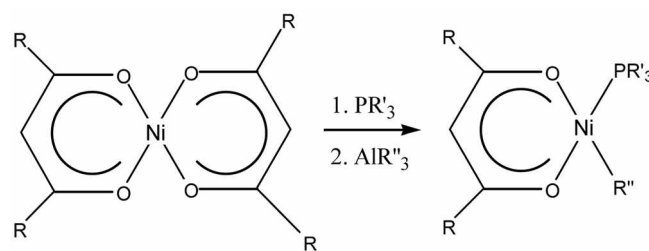
polymerizations proceed *via* homogeneous catalysis and substituents on 4 or 5 positions induce higher activities irrespective of their electronic nature. The activity was found to be dependent on the substituents, temperature, and solvents.

The orders of norbornene polymerization activities are as follows; MeO > F > Me₂ > NO₂ > Cl₂ > Me > H (in toluene), and F > NO₂ > MeO > Me₂ > Cl₂ > Me > H (in chlorobenzene). Even though the trends become inconsistent with

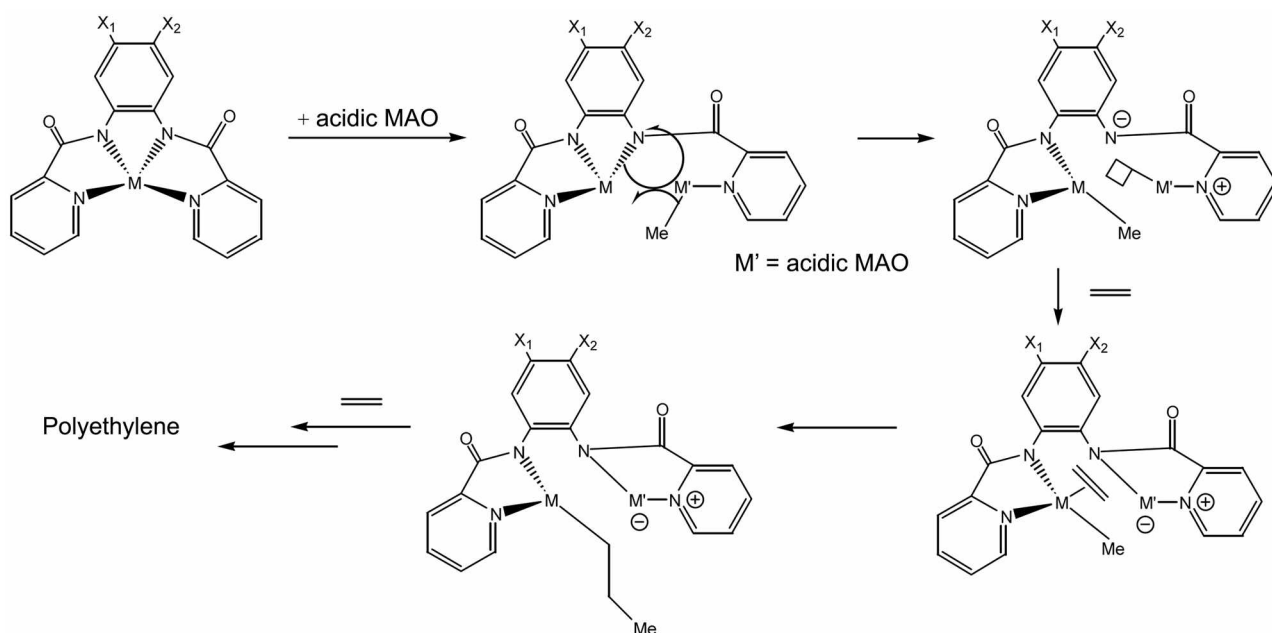
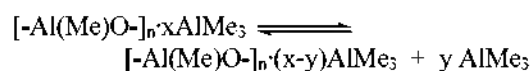
the change of solvents, catalysts with electron-withdrawing substituents generally show higher activities especially in polar solvent. In other words, electronic effects appear to be more significant in polar solvent.

Since the structures of these complexes are essentially square planar, these trends cannot be rationalized by the steric factor, either. Therefore, the higher activity observed in more polar solvent, chlorobenzene, led us to suggest the polar nature of the catalytically active intermediates.

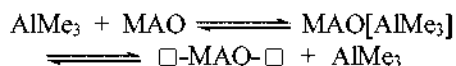
Since 4-coordinate active species are generally involved in the olefin polymerization catalyzed by many Ni and Pd complexes, the pathway containing 4-coordinate species seems to be reasonable. Since alkyl olefin cationic complexes are generally considered as the catalyst resting state in the late transition metal catalyst system,^{13c} but no detailed mechanisms in the systems which are active for olefin polymerization despite of the absence of these ligands have been reported.¹⁸ In this regard, it is worth mentioning that alkyl complex was formed by the reaction of alkylaluminum in the presence of phosphines as described in the following reaction.¹⁹



It is known that trimethylaluminum (TMA) always remains together with MAO due to the equilibrium between "free" TMA and "associated" TMA.²⁰

**Scheme 3.** Proposed polymerization mechanism.

Zakharov also reported that the MAO interaction with free TMA could produce MAO species containing Al with more acidity that acts as an effective cocatalyst during the alkylation process.²¹



With these things in mind, we propose the olefin polymerization by our nickel complexes as shown in Scheme 2; one terminal pyridine may dissociate first by the reaction with acidic MAO to leave a vacant site and transfer of alkyl group from Al to Ni may follow to give a site for incoming olefin. Therefore, simple Lewis acids such as trialkylaluminums are expected to catalyze polymerization even though activities are not as high as MAO. However, addition of 400 equivalents of AlMe₃ or Al(*i*-Bu)₃ instead of MAO did not induce polymerization at all even after 24 hrs. This may be due to preferential coordination of dissociated imido anion and Lewis acidities of AlMe₃ or Al(*i*-Bu)₃ may not be enough to prevent this reaction. Dried MMAO also did not induce polymerization while dried MAO induced less and slower polymerization than normal MAO (MAO with free AlMe₃). Probably only MAO species with more acidity described above guarantees a vacant site for the incoming olefin by preferential combination with the dissociated imido ligand.

Higher activity in polar solvent can be interpreted by stabilization of the charged intermediate proposed in Scheme 2.

This process involving 4-coordinate species may be preferred since not much 5- or 6-coordinate nickel or palladium complexes are common,¹⁸ and there are rare examples for four-coordinate Pd or Ni complexes where addition of an extra ligand occurs.²¹ Therefore, higher activity is expected if the pyridine dissociate more easily. It may be postulated that the pyridine may dissociate more easily with the greater torsional angle (pyridine plane with respect to the N1/N2/N3/N4 plane). As expected, the torsional angle and activity for norbornene polymerization increases in the following order; F (9.04) > Cl₂ (7.98) > Me₂ (5.94). The much greater torsional angle (24) in the Me derivative, **12** than other values may be due to poor crystallinity and it was excluded in this trend. The lower activity for **3** may be due to lower solubility.

Higher activities induced by the presence of electron-withdrawing and -donating substituents in the phenyl ring cannot be rationalized in a simple manner. Electron-withdrawing groups would stabilize the anionic imido intermediate by resonance and induce higher activity. Electron-donating groups would increase electron density on the imido N atom leading easier dissociation and higher activity resulted in.

Also higher activity is expected if the pyridine dissociates more easily and we are actively working to find out the relationships between complex structure and activity, if any.

Induction period was also observed, which indicates that an active intermediate is slowly formed at the early stage of the reaction.

Activity of the complex increases with temperature up to 70 °C but decreases at 100 °C. This behavior represents

rather higher thermal stability of the catalysts, which is desirable in the industrial application, possibly due to increased chelate effect with rigid tetradentate ligands. Molecular weight of the polymer is also dependent on the nature of catalysts, solvents and temperature. No clear relationship between molecular weight and nature of substituents is also observed. Much higher molecular weight is found in the polymer obtained in chlorobenzene. This may be due to higher propagation rate than termination one in this solvent. As the temperature increases, the molecular weight decreases as expected. In toluene, PDI remains almost constant but increases significantly in chlorobenzene.

Finally, it is worth mentioning that PDI becomes larger with the increase of temperature especially in chlorobenzene, while molecular weights decrease as expected from the higher termination rates, indicating that many active species are formed probably due to partial decomposition. This may support that activity of these complexes with rigid tetradentate ligands originate from partial dissociation of ligands described in Scheme 2.

Conclusion

New Ni complexes containing novel tetradentate ligands, 4,5-substituted-1,2-bis(pyridine-2-carboxamide)benzene ligands but lacking terminal alkyl or halide ligands were activated with MMA to be proven as efficient catalysts for the polymerization of norbornene and ethylene. Both electron-donating and -withdrawing substituents on the benzene ring and polar solvents enhance the catalytic activity for olefin polymerization. Norbornene is much more easily polymerized than ethylene. Improvement in thermal stability of the complexes was also observed. Some of these complexes were crystallographically determined to have square planar geometry. Even though many trials to detect the active species were not successful yet, a plausible mechanism involving dissociation of ligands and rearrangement of a carbonyl group is proposed.

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Supplementary material: Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 240689, 240690, 240691, and 240692 for complexes **9**, **10**, **13**, and **12**. Copies of this information may be obtained free of the charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk, or <http://www.ccdc.cam.ac.uk>).

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