

Highly Active Neutral Nickel(II) Complexes Bearing P,N-Chelate Ligands: Synthesis, Characterization and Their Application to Addition Polymerization of Norbornene

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Neutral nickel(II) complexes $[[R-NP]NiPh(PPh_3)]$ (**1**, $R = H$; **2**, $R = CH_3$) bearing P,N-chelate ligands ($[H-NP] = (2\text{-diphenylphosphanyl})\text{benzenamine } L^1$; $[CH_3-NP] = (2\text{-diphenylphosphanyl})\text{-}N\text{-methylbenzenamine } L^2$) have been synthesized and characterized. The molecular structure of complex **1** has been confirmed by single-crystal X-ray analyses. After activation with methylaluminoxane (MAO), catalytic precursors **1** and **2** could polymerize norbornene to afford addition-

type polynorbornene (PNB) with very high activities ($4.43 \times 10^7 \text{ g-PNB mol}^{-1}\text{-Ni h}^{-1}$), high molecular weight M_w ($3.07 \times 10^6 \text{ g mol}^{-1}$) and moderate molecular weight distribution M_w/M_n . Catalytic activities, polymer yield, M_w and M_w/M_n of PNB have been investigated under various reaction conditions.

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Introduction

Various late transition metal complexes containing chelating ligands act as catalysts for the polymerization and oligomerization of olefins. Early work on the Shell Higher Olefin Process (SHOP)^[1] utilized neutral Ni catalysts containing P–O chelates. Subsequent work has investigated, mainly, several classes of ligands: $[O-P]^-$,^[2–6] $[O-N]^-$,^[7–16] $[N-N]^-$.^[17–23] P,N ligands have attracted increasing recent attention because of their bonding versatility with a metal center and the relative ease with which the electronic and steric properties of the donor atoms can be modified.^[24–26] Braunstein et al.^[27] reported a series of nickel complexes, containing P,N-chelate ligands, and their catalytic ethylene oligomerization behavior. Liang et al.^[28] have synthesized several metal complexes supported by bidentate diarylamido phosphane ligands.

Homo-polymer addition of polynorbornenes is of considerable importance because the products have interesting and unique properties, including high chemical resistance, good solubility in organic solvents, good UV resistance, low dielectric constant, high glass-transition temperature, excellent optical transparency, large refractive index, and low birefringence. However, the addition polymerization of norbornene was much less developed than ROMP (ring-opening metathesis polymerization). In 1993, Deming and Novak introduced the first nickel complex for the addition polymerization of norbornene.^[29] Several other catalyst sys-

tems have also been applied recently to this reaction.^[30,31d]

Following our research on neutral nickel complexes,^[16,31] we synthesized neutral nickel(II) complexes with a chelating P,N ligands and firstly investigated their catalytic norbornene addition polymerization behaviors. These neutral nickel(II) complexes have very high activities for cyclo-olefin polymerization. This article focuses on the syntheses of neutral nickel(II) complexes **1** and **2** bearing P,N-chelate ligands and the polymerization of norbornene upon activation with methylaluminoxane (MAO). The typical molecular structure of catalytic precursor **1** was characterized by an X-ray crystallographic study. To the best of our knowledge, neutral nickel(II) complexes bearing P,N-chelate ligands for the addition polymerization of norbornene have been scarcely investigated.

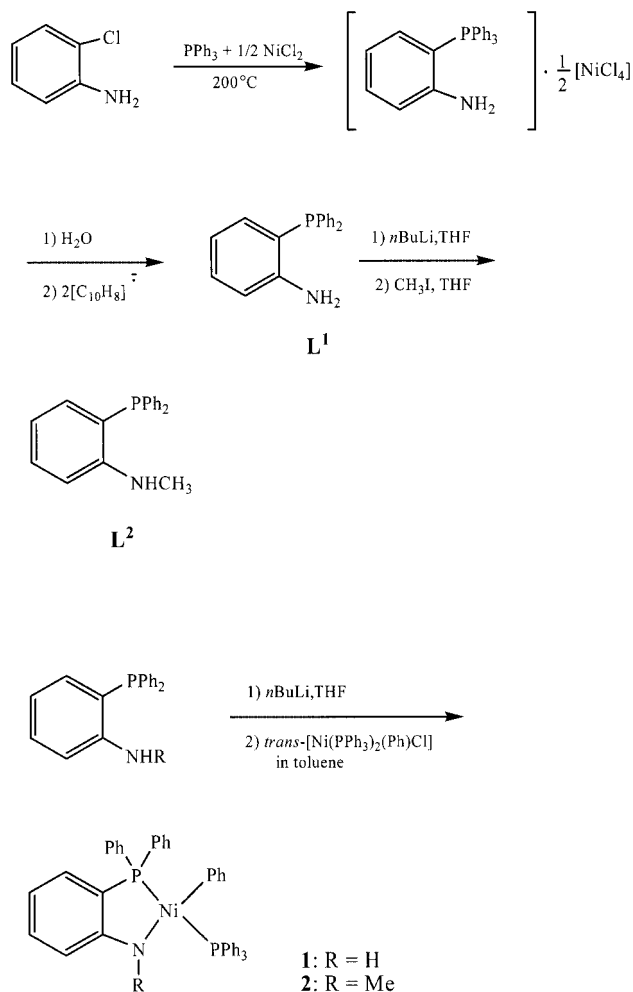
Results and Discussion

Syntheses of Ligands and Complexes

Syntheses of complexes **1** and **2** are outlined in Scheme 1. (2-Diphenylphosphanyl)benzenamine (ligand **L**¹) was prepared according to literature methods.^[36] Ligand **L**² [(2-diphenylphosphanyl)-*N*-methylbenzenamine] was synthesized by monolithiation of the NH_2 group of ligand **L**¹ with *n*BuLi (1.0 equiv.), followed by the addition of CH_3I (1.0 equiv.). After workup, **L**² was extracted with hot hexane and obtained after evaporation of solvent as a white solid.

Ligands **L**¹ and **L**² were treated with *n*BuLi in THF and then treated with *trans*-chloro(phenyl)bis(triphenylphosphane)nickel(II) to give complexes **1** and **2**, respectively. Both complexes were purified by recrystallization from tol-

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Scheme 1. Syntheses of nickel complexes **1** and **2**.

uene. All compounds were well characterized by ^1H NMR, FT-IR as well as elemental analysis.

Single Crystal X-ray Structure Analyses of Complex **1**

A single crystal of **1** suitable for X-ray diffraction study was grown from a concentrated CH_2Cl_2 solution at -30°C . Table 1 summarizes the collection and refinement data of the analyses. Figure 1 shows the ORTEP diagram of **1**. Complex **1** contains a chelating [P,N] ligand, a triphenylphosphane group (PPh_3) and a phenyl group. The bulky diphenylphosphane moiety occupies the position trans to PPh_3 , with a nearly linear $\text{P}(1)\text{--Ni}(1)\text{--P}(2)$ angle of $173.97(3)^\circ$, and the phenyl group attached to Ni lies trans to $\text{N}(1)$, with a $\text{C}(19)\text{--Ni}(1)\text{--N}(1)$ angle of $172.80(10)$. The *cis* angles at nickel are in the range $84.44\text{--}95.83^\circ$. Thus, the nickel center lies perfectly on the square plane defined by the four donor atoms. In addition, the metal ion deviates from the $[\text{P}(1), \text{N}(1), \text{P}(2)$ and $\text{C}(19)]$ plane by ca. $0.0828 \text{ \AA}$.

Table 1. Crystal data and summary of data collection and refinement details for **1**.

Formula	$\text{C}_{42}\text{H}_{35}\text{NNiP}_2$
Formula mass	674.36
Crystal system	monoclinic
Space group	$P2_1/c$
<i>a</i> [Å]	16.011(4)
<i>b</i> [Å]	9.916(2)
<i>c</i> [Å]	21.824(5)
<i>V</i> [Å ³]	3448.2(14)
β [°]	95.634(3)
<i>Z</i>	4
Color	red
Crystal size [mm]	$0.20 \times 0.10 \times 0.08$
$D_{\text{calcd.}}$ [g cm ⁻³]	1.299
μ [mm ⁻¹]	0.686
θ limits [°]	1.28/26.01
λ [Å]	$\text{Mo-K}\alpha$ (0.71073)
<i>F</i> (000)	1408
No. of obsd. reflections	6745
No. of parameters refined	415
$R_1[I > 2\sigma(I)]$	0.0379
$wR_2(\text{all data})$	0.0806
GOF on F^2	0.859

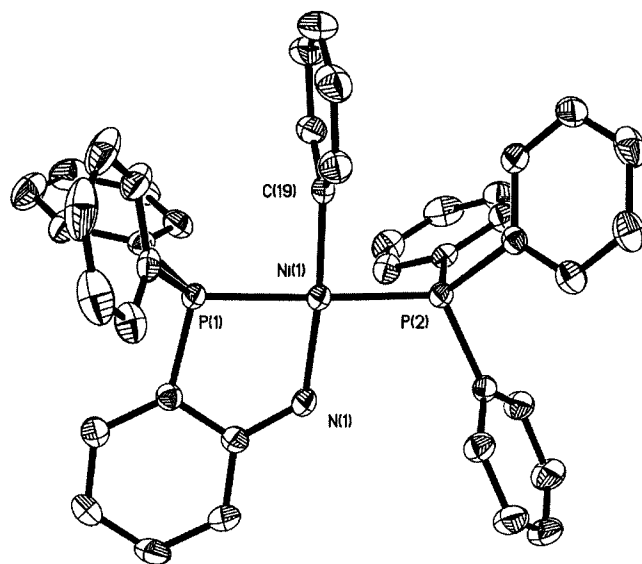


Figure 1. Molecular structure of complex **1**. Selected bond lengths [Å] and angles [°]: $\text{Ni}(1)\text{--N}(1) = 1.892(2)$, $\text{Ni}(1)\text{--C}(19) = 1.910(2)$, $\text{Ni}(1)\text{--P}(1) = 2.1670(9)$, $\text{Ni}(1)\text{--P}(2) = 2.1999(9)$, $\text{P}(1)\text{--C}(6) = 1.795(3)$, $\text{N}(1)\text{--C}(1) = 1.366(3)$; $\text{N}(1)\text{--Ni}(1)\text{--C}(19) = 172.80(10)$, $\text{N}(1)\text{--Ni}(1)\text{--P}(1) = 84.44(7)$, $\text{C}(19)\text{--Ni}(1)\text{--P}(1) = 89.23(8)$, $\text{N}(1)\text{--Ni}(1)\text{--P}(2) = 95.83(7)$, $\text{C}(19)\text{--Ni}(1)\text{--P}(2) = 90.83(8)$, $\text{P}(1)\text{--Ni}(1)\text{--P}(2) = 173.97(3)$.

Addition Polymerization of Norbornene

Preliminary experiments indicated that complexes **1** and **2** can not catalyze ethylene polymerization with or without methylaluminoxane (MAO) as co-catalyst at 10 atm of ethylene. However, after activation with MAO, they could catalyze the polymerization of norbornene to afford addition-type polynorbornene (PNB) with high activities ($10^7 \text{ g-PNB mol}^{-1}\text{-Ni h}^{-1}$), high molecular weight M_w (10^6 g mol^{-1}) and moderate molecular weight distributions M_w/M_n (2.65–3.93). Complexes **1** and **2** themselves and MAO did not

Table 2. Addition polymerization of norbornene with nickel complexes **1** and **2** activated by methylaluminoxane (MAO).^[a]

Entry	Complex	Amount of cocat [equiv.]	Polymer [g]	Activity ^[b]	M_w ^[c]	M_w/M_n ^[c]
1	1	500	Trace	–		
2	1	1000	1.05	3.14	2.71	3.40
3	1	2000	1.13	3.39	2.61	3.20
4	1	3000	1.30	3.90	2.57	2.72
5	1	4000	1.12	3.36	2.06	2.65
6	1	5000	1.06	3.18	2.88	2.32
7	1	10000	1.03	3.09	3.07	2.58
8 ^[d]	1	–	trace	–		
9	2	3000	0.942	2.83	2.46	3.93
10	2	4000	0.808	2.42	2.28	3.81
11 ^[d]	2	–	trace	–		
12 ^[e]	–	3000	trace	–		

[a] Polymerization conditions: solvent, chlorobenzene; total volume 10 mL; nickel complex (0.2 μmol), norbornene (1.88 g) [norbornene:nickel (molar) = 100 000]; reaction time 10 min; 30 °C. [b] 10^7 g-PNBmol^{−1}·Ni h^{−1}. [c] M_w (10^6 g mol^{−1}) and M_w/M_n determined by GPC. [d] Without co-catalyst MAO. [e] Without nickel complex.

produce polymers under the same conditions (entries 8, 11, 12 in Table 2). In general, the steric structure and bulky group in the nickel complexes slightly influence the catalytic activities. Moreover, the addition mechanism of norbornene, when using neutral nickel complexes, has been hypothesized as the insertion of norbornene into the Ni–C bond.^[30i,30j] Thus, the N-methyl group of complex **2** makes the insertion of norbornene into the Ni–C bond more difficult than H of complex **1**, so complex **2** displays lower catalytic activity than complex **1**.

To investigate the reaction parameters affecting addition polymerization of norbornene, the catalytic precursor **1** was studied under different reaction conditions. MAO was essential for the polymerization of norbornene catalyzed by **1** and **2**. It initiates the polymerization of norbornene and probably creates an empty site for insertion of the norbornene monomer. Varying the MAO:complex **1** ratio (expressed here as Al:Ni ratio) had considerable effects on catalytic activity and M_w . The activity of **1** is almost zero for Al:Ni = 500 (entry 1, Table 2), but is up to 10^7 g-PNBmol^{−1}·Ni h^{−1} when Al:Ni > 1000. The catalytic activities of complex **1** increase first and then decrease with increasing Al:Ni ratio; the activity is highest at Al:Ni = 3000. The M_w of polymers also exhibits remarkable changes with Al:Ni, and is lowest at Al:Ni = 4000.

The reaction temperature also affects considerably the catalytic activities and M_w (Table 3). With increasing reaction temperature, the catalytic activities first increase and then decrease – the highest activity is at 30 °C (3.90×10^7 g-PNBmol^{−1}·Ni h^{−1}). In contrast, M_w decreased with increasing temperature while M_w/M_n varied irregularly.

Figure 2 reveals the effects of reaction time on catalytic activities and polymer yields. The yields of PNB gradually increase with increasing reaction time, but the catalytic activities of complex **1** always decrease. After 1 h, the yield is almost up to 90%, but the activity has reduced to 10^6 g-PNBmol^{−1}·Ni h^{−1}.

The concentration of norbornene also exerts a considerable influence on the polymerization reaction (Figure 3). The catalytic activity of complex **1** increases almost linearly with monomer concentration in the range 0.5–2.5 mol L^{−1},

Table 3. Influence of the reaction temperature (T) on activities of complex **1**.

Entry	T [°C]	Polymer [g]	Activity ^[a]	M_w ^[b]	M_w/M_n
1	0	0.309	0.927	2.80	3.23
2	30	1.30	3.90	2.57	2.72
3	60	1.08	3.24	1.81	2.67
4	90	0.799	2.40	1.37	2.89

[a] 10^7 g-PNBmol^{−1}·Ni h^{−1}. [b] M_w (10^6 g mol^{−1}). Polymerization conditions: solvent, chlorobenzene; total volume 10 mL, nickel complex (0.2 μmol), norbornene (1.88 g) [norbornene:nickel(molar) = 100000]; MAO (0.35 mL, 1.7 M) [Al:Ni = 3000]; reaction time 10 min.

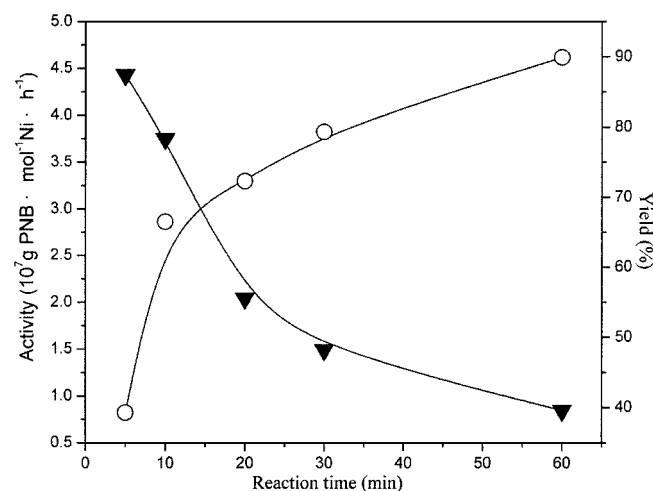


Figure 2. Activity (▲) and yield (○) vs. reaction time; 0.2 μmol complex **1**, norbornene:nickel(molar) = 100 000, Al:Ni = 3000, V_{total} = 10 mL, polymerization at 30 °C.

and then remains nearly constant when the concentration exceeds 3.0 mol L^{−1}.

The crystallinity of the resultant polymers was investigated by XRD. Figure 4 shows the XRD diagram of the obtained PNB. Two broad halos at 2θ of 11 and 18° are present. This pattern is predominantly intrachain, probably corresponding to a short-range order, or to a pseudo-periodicity arrangement of the bicycle units along the chain.

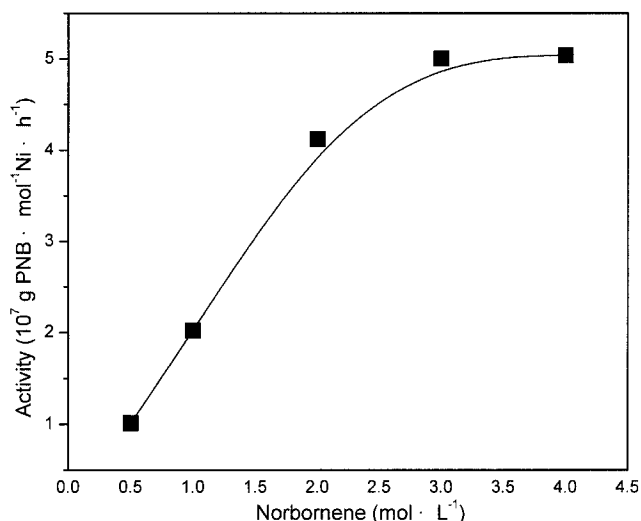


Figure 3. Activity vs. norbornene concentration; 0.2 μmol complex **1**, Al:Ni = 3000, V_{total} = 10 mL, polymerization at 30 °C for 10 min.

This is almost in agreement with reported results.^[32,33] No traces of Bragg reflections, characteristic of crystalline regions, are revealed. The PNB is therefore, non-crystalline.

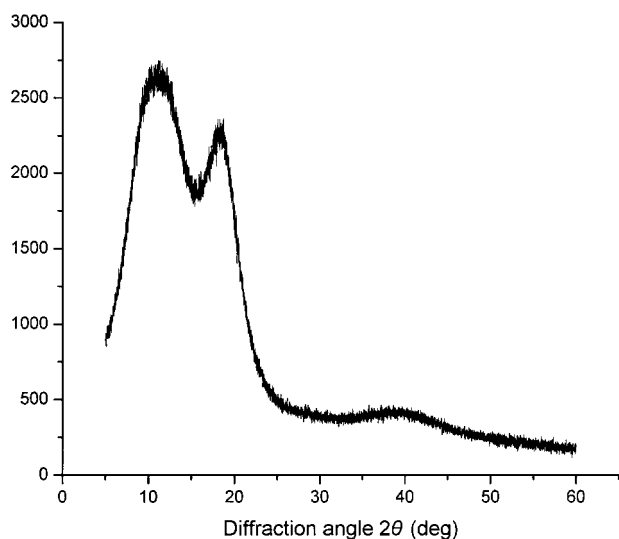


Figure 4. XRD diagram of PNB.

All polymers obtained showed very similar IR and ^1H NMR spectra. ^1H NMR spectra exhibited no trace of the double bond that is typical for ROMP polynorbornene.^[34,30] PNB resonances appear at 0.9–2.6 (m, maxima at 1.3, 1.5, 1.7, 2.4 ppm). A double bond, which is often seen at 1680–1620 cm^{-1} , was also absent from the IR spectra. The glass transition temperature (T_g) of addition-type homo-polynorbornene has proved difficult to obtain since it is, apparently, close to the temperature at which decomposition tends to set in.^[35] Our attempts to determine the T_g of PNB also failed, and DSC studies did not give an endothermic signal upon heating to the decomposition temperature (above 450 °C).

Conclusions

(2-Diphenylphosphanyl)benzenamine (**L**¹) and (2-diphenylphosphanyl)-*N*-methylbenzenamine (**L**²) were prepared in good yields for the syntheses of neutral nickel(II) complexes **1** and **2**. Complex **1** was characterized by single-crystal X-ray diffraction. Both complexes showed high catalytic activities for the addition polymerization of norbornene after activation with MAO. Catalytic activities of up to $4.43 \times 10^7 \text{ g-PNB mol}^{-1} \text{ Ni h}^{-1}$ and M_w up to $3.07 \times 10^6 \text{ g mol}^{-1}$ were observed. Activities, polymer yield and M_w can be controlled by varying the reaction parameters. PNBs obtained here are amorphous and soluble in halogenated aromatic hydrocarbons. Therefore, neutral Ni^{II} complexes with chelating P,N ligands are, perhaps, a promising system for the addition polymerization of norbornene. We are currently working to develop new P-N nickel complexes for the polymerization of norbornene.

Experimental Section

General Remarks: All manipulations of air- and/or water-sensitive compounds were performed under dry nitrogen using standard Schlenk and vacuum-line techniques. Solvents were dried by boiling under reflux with appropriate drying agents and distilled under nitrogen before use. (2-Diphenylphosphanyl)benzenamine^[36] and *trans*-[Ni(PPh₃)₂(Ph)Cl]^[37] were prepared according to literature procedures. Norbornene (bicyclo[2.2.1]hept-2-ene, Acros) was purified by distillation over sodium and used as a chlorobenzene solution. Methylaluminoxane (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 spectra were recorded with a Nicolet-FT-IR-50X spectrometer. NMR spectroscopic data for PNB were obtained at ambient temperature with a Bruker AC 500 spectrometer instruments using [D₄]-*o*-chlorobenzene as solvent. Average molecular weight (M_w) and molecular weight distributions (M_w/M_n) of PNB products were determined using a PL GPC-220 gel permeation chromatograph at 150 °C, employing narrow standards calibration, and equipped with three PL gel columns (sets of PL gel 10 m MIXED-B LS). Trichlorobenzene was used as solvent at a flow rate of 1.00 mL min⁻¹. Differential scanning calorimetric (DSC) measurements were performed with a Perkin-Elmer Pyris 1 DSC. The X-ray diffraction (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°.

Synthesis of Ligand L²: A solution of ligand **L**¹ (0.555 g, 2.0 mmol) in THF (20 mL) was cooled to -78 °C and *n*BuLi was then added slowly (1.0 equiv., 0.87 mL, 2.3 M, 2.0 mmol). After the solution was stirred for 1 h at -78 °C, CH₃I (1.0 equiv., 0.125 mL, 2.0 mmol) was slowly added at -78 °C. The reaction mixture was then stirred for 2 h at -78 °C and warmed to room temperature overnight. The solution was hydrolyzed with degassed water (5 mL) and extracted with diethyl ether (3 × 3 mL). Finally, the organic phase was separated, dried over degassed MgSO₄, and filtered. After evaporation of the diethyl ether, the product was isolated as a white solid (yield 0.456 g, 1.56 mmol, 78%). ^1H NMR (CDCl₃): δ = 2.82 (s, 3 H, N-

CH₃), 6.65 (m, 2 H, *m*-H of P), 6.75 (m, 1 H, *p*-H of P), 7.34–7.23 (m, 11 H, Ar-H) ppm.

Synthesis of Complex 1: A solution of ligand **L**¹ (0.277 g, 1.0 mmol) in THF (15 mL) was cooled to –78 °C, and *n*BuLi was added dropwise (1.0 equiv., 0.48 mL, 2.3 M, 1.0 mmol). This mixture was allowed to warm to room temperature and then stirred for 2 h to afford the lithium salt of **L**¹. After evaporation of THF under vacuum, the lithium salt of **L**¹ was dissolved in toluene (10 mL). The resultant solution was slowly channeled into a 50 mL flask with *trans*-[Ni(PPh₃)₂(Ph)Cl] (0.668 g, 0.96 mmol) in toluene (10 mL) and continuously stirred overnight at room temperature. The resultant reaction mixture was then separated by centrifugation to remove LiCl. After the upper clear dark red solution was concentrated to about 3 mL, hexane (20 mL) was added and complex **1** was obtained as a red-orange solid (yield 0.499 g, 77%). Red single crystals suitable for X-ray were recrystallized from CH₂Cl₂ at –30 °C. C₄₂H₃₅NP₂Ni (674.39): calcd. C 74.80, H 5.23, N 2.08; found C 74.46, H 5.25, N 1.93. ¹H NMR (CDCl₃): δ = 7.93–7.27 (m, 34 H, Ar-H) ppm.

Synthesis of Complex 2: A dark red powder of complex **2** was obtained in a manner similar to that for complex **1** (yield of 68%, 0.449 g). C₄₃H₃₇NP₂Ni (688.42): calcd. C 75.02, H 5.42, N, 2.03; found C 74.76, H 5.18, N 1.98. ¹H NMR (CDCl₃): δ = 2.79 (s, 3 H, N-CH₃), 7.91–7.26 (m, 34 H, Ar-H) ppm.

Structure Solution and Refinement for Complex 1: For **1**, a single crystal suitable for X-ray analysis was sealed in a glass capillary, and the intensity data of the single crystal were collected with a CCD-Bruker Smart APEX system. All determinations of the unit cell and intensity data were performed with graphite-monochromated Mo-*K*_α radiation (λ = 0.71073 Å). All data were collected at room temperature using the ω scan technique. Structures were solved by direct methods, using Fourier techniques, and refined on *F*² by a full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included but not refined. Crystallographic data are summarized in Table 1.

CCDC-252436 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Polymerization of Norbornene: In a typical procedure (entry 4, Table 2), nickel complex **1** (0.2 μmol) in chlorobenzene (1.0 mL), norbornene (1.88 g) in chlorobenzene (3.0 mL) and another 3.0 mL of fresh chlorobenzene were added to a special polymerization bottle (20 mL) with strong stirrer under nitrogen. After keeping the mixture at 30 °C for 10 min, MAO (0.35 mL) was added to the polymerization system via syringe and the reaction was initiated. Ten minutes later, acidic ethanol (*V*_{ethanol}:*V*_{conc.HCl} = 20:1) was added to terminate the reaction. The PNB produced 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 (achieved by varying the amount of chlorobenzene when necessary). IR (KBr): ν̄ = 2950, 2865, 1475, 1453, 1294, 1257, 1220, 1189, 1142, 1105, 937, 890 cm^{–1}. ¹H NMR: δ = 0.9–2.6 (m, maxima at 1.3, 1.5, 1.7, 2.4 ppm).

Acknowledgments

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