Synthesis and Characterization of Pyrrole-imine [N⁻NP] Nickel(II) and Palladium(II) Complexes and Their Applications to Norbornene Polymerization

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Ni(II) and Pd(II) complexes based on *N*-((1*H*-pyrrol-2-yl)methylene)-2-(diphenylphosphino)benzenamine were synthesized and characterized. X-ray diffraction studies on complexes **1**, **2**, and **4** revealed that N, N, P, and halogen atoms coordinated to metal, with distorted square planar geometries in all cases. Upon treatment with modified methylaluminoxane (MMAO), the [N⁻NP]Ni(II)X complexes are robust and exhibit high activity for the vinyl addition polymerization of norbornene (up to 5.46×10^7 g PNB/mol(Ni)·h·atm).

Introduction

During the last decades, there have been tremendous advances in the field of homogeneous late-transition metal catalysts for olefin polymerization.[1] For example, the families of nickel and palladium complexes,[2–4] such as those based on α-diimine[2a] or salicylaldimine,[2b,2c] have proven to be one of the most efficient precatalysts. In the presence of MMAO, α-diimine nickel and palladium complexes could catalyze the polymerization of ethylene or propylene with high activities to give linear to highly branched or even to dendritic polymers.[2a,e,3c,d] Palladium complexes could promote the copolymerization of ethylene with polar comonomers such as methyl acrylate effectively.[2d,f,g,3a,b,e,f] Salicylaldiminato nickel(II) complexes were reported to polymerize ethylene in the presence of functional additives.[2c] Recently, some nickel and palladium complexes were also found to be highly active for the polymerization of norbornene,

affording vinyl-addition polymers with molecular weights higher than 10^6 g/mol.[4] Of the Ni(II) and Pd(II) precatalysts developed,[2–5] most are involved in bidentate ligand-derived complexes. A few complexes based on tridentate ligands were reported for this purpose except limited examples related to oligomerization of ethylene.[4a,g,n,5] Of them, Braunstein et al. described that a [NPN] nickel complex could be used to promote oligomerization of ethylene with a TOF up to 37 900 in the presence of 6 equiv of AlEtCl₂.[5a] Carpentier and Casagrande et al. documented that tridentate pyrazolyl nickel complexes were highly efficient catalysts for the dimerization of ethylene with a selectivity up to 92% for the 1-butene fraction.[5b] Several 2,6-bis(imino)pyridine nickel complexes were synthesized.[5c,d] These nickel complexes either proved to be inert to ethylene polymerization or showed low activity (5×10^3 g/mol(Ni)·h·atm) for the dimerization of ethylene. As our ongoing research project on synthesis and applications of metal complexes based on tridentate ligands in asymmetric synthesis[6] and olefin polymerization,[7] very recently, we designed and synthesized *N*-((1*H*-pyrrol-2-yl)methylene)-2-(diphenylphosphino)benzenamine (**L1**) and the cor-

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Scheme 1. Synthesis of Complexes 1−4

M = Ni, X = Cl, **1**
M = Ni, X = Br, **2**
M = Ni, X = I, **3**
M = Pd, X = Cl, **4**
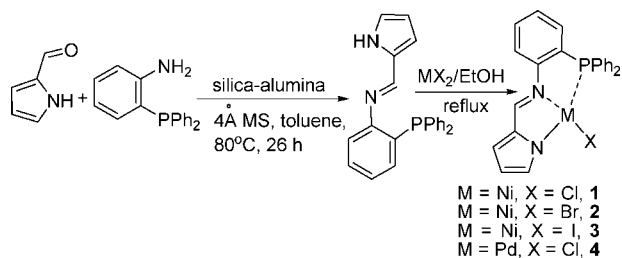
responding nickel−palladium complexes. It was found that the nickel complexes could catalyze the polymerization of norbornene with activity up to 5.46×10^7 g PNB/mol(Ni)·h·atm in the presence of MMAO. In this paper, we wish to report the results in detail.

Results and Discussion

Ligand and Complex Synthesis. Complexes **1−4** were synthesized as shown in Scheme 1. Pyrrole-imine ligand **L1** was prepared readily by the condensation of 2-(diphenylphosphino)aniline and pyrrole-2-carboxaldehyde in the presence of silica–alumina 135 and 4 Å molecular sieves.[8] Treatment of pyrrole-imine ligand **L1** with anhydrous NiX_2 or $PdCl_2$ in anhydrous ethanol under reflux afforded the desired complexes in 41–80% yields. In the solid state, complexes **1**, **2**, and **4** are stable in air. Iodide **3** should be kept in the dark to avoid its decomposition.

All the complexes were well characterized by FT-IR, elemental analyses, ^{1}H NMR, and mass spectral analysis. The C=N vibration absorption in IR spectra of complexes **1−4** exhibited a characteristic shift from 1619 cm^{-1} (free ligand) to 1547–1552 cm^{-1} (complexes), suggesting that the nitrogen atoms of the imine groups coordinate to metal. The molecular structures of complexes **1**, **2**, and **4** were further confirmed by single-crystal X-ray analyses (Figures 1−3). As shown in Figure 1, nickel complex **1** adopts a distorted square planar geometry around nickel(II). The N(1), N(2), P, and Cl atoms are nearly coplanar, with Cl and N(2) occupying the trans position (Cl−Ni−N(2) angels of 176.9°, N(1)−Ni−P: 169.54°). The bond length of P−Ni (2.1458(2) Å) is shorter than that of the reported salicylaldiminato nickel(II) complex (P−Ni 2.172 Å).[2b] Noticeably, the Ni−N(1) bond and Ni−N(2) bond lengths are virtually identical (Ni−N(1) = 1.888(5) Å and Ni−N(2) = 1.886(3) Å), together with the fact of the longer C(4)−N(1) bond length in the pyrrole ring than the C(1)−N(1) bond (C(4)−N(1) = 1.363(7) Å vs C(1)−N(1) = 1.328(7) Å), suggesting electron delocalization in the N(1)−C(4)−C(5)−N(2) system. This is different from that of the pyrrolidine-imine based
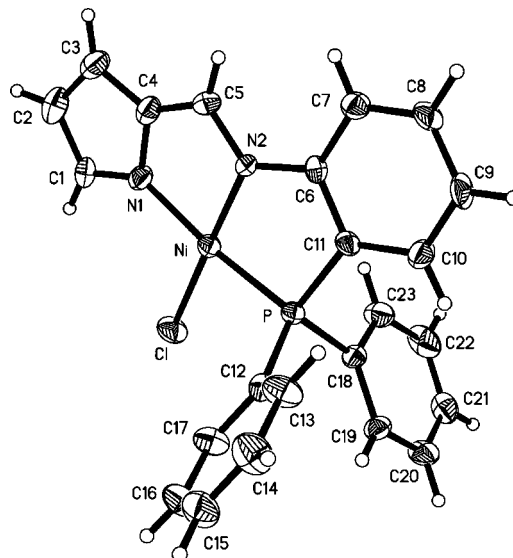

Figure 1. Molecular structure of complex **1**. Selected bond length (Å) and angles (deg): Ni−N(1) = 1.888 (5), Ni−N (2) = 1.886 (3), Ni−P = 2.1458 (2), Ni−Cl = 2.1628 (1), N(1)−Ni−N(2) = 83.8 (2), N(1)−Ni−P = 169.54 (2), N(2)−Ni−P = 86.3 (2), N(1)−Ni−Cl = 95.73 (2), N(2)−Ni−Cl = 176.9 (2), P−Ni−Cl = 94.30 (8).
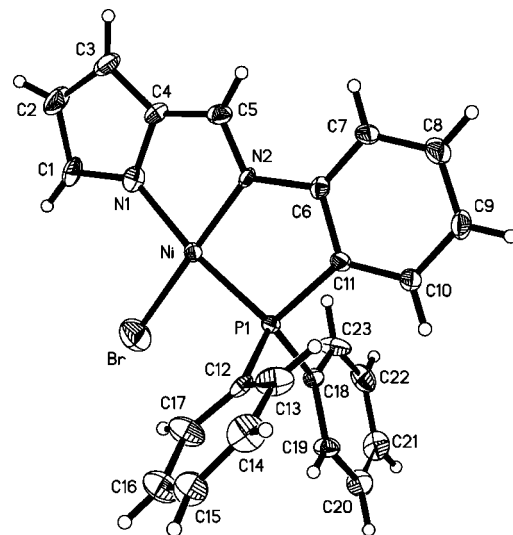

Figure 2. Molecular structure of complex **2**. Selected bond length (Å) and angles (deg): Ni−N(1) = 1.884(9), Ni−N(2) = 1.874(6), Ni−P(1) = 2.150(3), Ni−Br = 2.2304(16), N(1)−Ni−N(2) = 82.4(4), N(1)−Ni−P = 169.0(3), N(2)−Ni−P = 87.3(3), N(1)−Ni−Br = 96.9(3), N(2)−Ni−Br = 175.7(3), P−Ni−Br = 93.65(8).

titanium complexes reported by Fujita,[9] in which the length of the Ti−N (in pyrrole) bond is much shorter than that of the Ti−N bond (in the imine group) (2.033 and 2.185 Å, respectively).

The molecular structure of complexes **2** and **4** (Figures 2 and 3) are similar to that of complex **1**, both with a distorted square planar geometory with N(1), N(2), P, Br(Cl), and the metal atom being nearly coplanar. However, the bond lengths of C(1)−N(1) and C(4)−N(1) in pyrrole, which are different in complex **1** (C(1)−N(1) = 1.328 (7) Å vs C(4)−N(1) = 1.363 (7) Å), are

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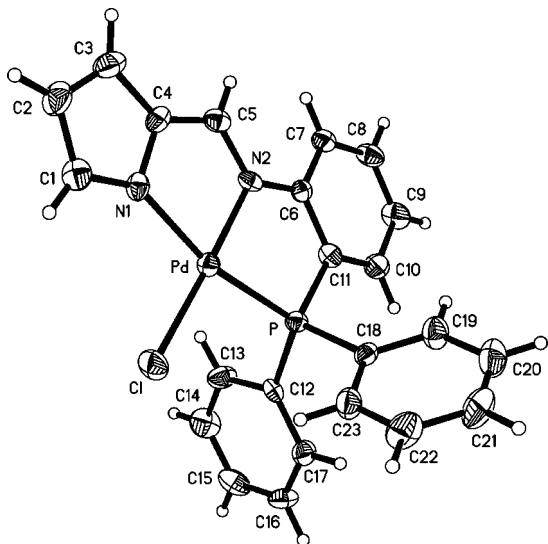
Figure 3. Molecular structure of complex **4**. Selected bond length (Å) and angles (deg): Pd−N(1) = 2.043(4), Pd−N(2) = 2.007(3), Pd−P = 2.2094(1), Pd−Cl = 2.2925(1), N(1)−Pd−N(2) = 81.2(2), N(1)−Pd−P = 165.47(1), N(2)−Pd−P = 84.58(2), N(1)−Pd−Cl = 97.80(1), N(2)−Pd−Cl = 177.3(2), P−Pd−Cl = 96.57(6).

almost the same in complex **2** (C(1)−N(1) = 1.388 (13) Å vs C(4)−N(1) = 1.392 (14) Å). Noticeably, the lengths of Ni(Pd)−N(imine) bonds are shorter than those of Ni(Pd)−N(pyrrole) bonds in all cases, and the difference is in the order of **1** (0.002 Å) < **2** (0.010 Å) < **4** (0.036 Å). Attempts to develop crystals of complex **3** suitable for X-ray analysis failed.

Norbornene Polymerization. In the presence of MMAO, nickel and palladium complexes **1**−**4** proved to be inactive to catalyze the polymerization of ethylene either at 50 °C, 1 atm or at 30 °C, 10 atm. However, complexes **1**−**3** could promote the polymerization of norbornene (NB) very well. For example, it was found that polynorbornene (PNB) generated immediately after MMAO was added to a mixture of norbornene and nickel complex in CH_2Cl_2 or $ClCH_2CH_2Cl$. Further study showed that the polymerization conditions strongly influenced the activities. As shown in Table 2, increasing the initial concentration of norbornene resulted in an improvement of activity from 1.49×10^7 g PNB/mol(Ni)·h·atm to 4.72×10^7 g PNB/mol(Ni)·h·atm (entries 1−3). The activities decreased with the prolongation of the polymerization time probably due to poor solubility of the quickly formed polymer in dichloromethane (DCM), which might block catalytic species (entries 2 and 4−6). Al/M molar ratios were also influenced strongly by the polymerization behaviors. For example, with the increase of the ratio from 100 to 2000, the activity was enhanced nearly four times (entries 2 and 7−9). Noticeably, high activity (1.1×10^7 g PNB/mol(Ni)·h·atm) was still observed in the presence of low Al/M molar ratio (Al/M molar ratio: 100), indicating that the stability of the active species was quite good. Solvents also strongly influenced the activity probably due to the solubility of complex **1** in the solvents. For example, both PhCl and $CHCl_3$ gave lower activity than DCM, and only a trace amount of polymer was observed in toluene (entries 2 and 15−17). 1,2-Dichloroethane (1,2-DCE) proved to be the optimal one. Under similar conditions in 1,2-DCE, 91% conversion of norbornene was achieved, and the activity was improved to 5.46×10^7 g PNB/mol(Ni)·h·atm. Control experiments showed that no polymers were produced in the absence of MMAO or complex **1**. Molecular weights of the produced PNB were slightly influenced by reaction conditions. In all cases determined, high M_w's

(around 1.8×10^6 g/mol) with very narrow molecular weight distributions between 1.12 and 1.31 were observed, suggesting that a single sitelike catalyst be formed.

Under the optimized conditions, the behavior of complexes **1**−**4** on norbornene polymerization were examined (Table 3). As shown in Table 3, nickel complexes **1**−**3** were highly active, and the anion of the complexes had a great effect on both conversions and activities. Nickel chloride **1** proved to be the most active (5.46×10^7 g PNB/mol(Ni)·h·atm, 91% conversion, entry 1). The activities and conversions diminished when both bromide **2** and iodide **3** were used instead of the chloride (entries 1−3, Table 3). Despite the different activity, all PNB produced by complexes **1**−**3** have high M_w (10^6 g/mol), very narrow PDI (1.24–1.27), and high TGA (>453 °C). The ^1H NMR and ^{13}C NMR analysis showed no signal of double bonds in the polymers, indicating that the polymers were norbornene adducts through vinyl-addition polymerization. Compared with the high activities exhibited by nickel complexes **1**−**3**, their palladium analogue **4** was found nearly inert toward norbornene polymerization (entry 4).

There are two possible pathways for this polymerization. One is that the polymerization proceeds via a vinyl-addition and another is via a cationic process. We found that complex **1**, after treating with AgOTf and $AgBF_4$, respectively, could not promote this polymerization at all in the absence of MMAO (Scheme 2). These results suggested that the cationic process is less possible, and we proposed this polymerization proceeded via vinyl-addition.

Conclusions

Nickel(II) and palladium(II) complexes based on *N*-((1*H*-pyrrol-2-yl)methylene)-2-(diphenylphosphino)benzenamine (**L1**) have been synthesized and characterized. The X-ray diffraction studies reveal that these complexes feature a distorted square planar coordination of the central metal with the N, N, and P atoms. In the presence of methylaluminoxane (MMAO), an activity of up to 5.46×10^7 g PNB/mol(Ni)·h·atm has been achieved with nickel complexes for the polymerization of norbornene. Further investigations into the polymerization mechanism are in progress in our laboratory.

Experimertal Section

General Information. All experiments involving air- and/or moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk techniques. ^1H NMR, ^{13}C NMR, and ^{31}P NMR were recorded on a Varian Mercury 300 spectrometer. Mass spectra were carried out with a HP5989A spectrometer. IR spectra were recorded using a Nicolet AV-360 spectrometer. Elemental analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). High-temperature gel permeation chromatography (GPC) was performed on Waters Alliance GPC 2000 in 1,2,4-trichlorobenzene at 135 °C using polystyrene calibration. Modified methylaluminoxane (MMAO) was purchased from Akzo Nobel with 7 wt % Al (1.9 M) in toluene. Toluene was distilled under nitrogen over sodium-benzophenone. Norbornene was refluxed over Na and distilled. CH_2Cl_2 and $ClCH_2CH_2Cl$ were dried over CaH_2. Ethanol was purified prior to use. 2-(Diphenylphosphino)aniline was synthesized according to the literature methods.[10]

X-Ray Structure Determination. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo K (λ

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Table 1. Crystal Data and Summary of Data Collection and Refinement Details for 1, 2, and 4

	1	**2**	**4**
formula	$C_{23}H_{18}N_2ClPNi$	$C_{23}H_{18}BrN_2NiP$	$C_{23}H_{18}N_2PClPd$
crystal size (mm)	0.36 × 0.23 × 0.04	0.32 × 0.13 × 0.06	0.33 × 0.16 × 0.11
fw	447.52	491.98	495.21
crystal system	Orthorhombic	Orthorhombic	Orthorhombic
space group	*Pna2(1)*	*Pna2(1)*	*Pna2(1)*
a, Å	18.7870(18)	18.8941(17)	18.8885(13)
b, Å	8.8927(9)	8.8776(8)	8.9493(7)
c, Å	11.8928(12)	11.9195(11)	11.9998(9)
V, Å^3	1986.9(3)	1999.3(3)	2028.4(3)
Z	4	4	4
D_{calcd}, Mg/m^3	1.496	1.634	1.622
2θ range, deg	4.34 to 56.52	4.32 to 51.98	4.32 to 56.56
μ, mm^{-1}	1.202	3.060	1.136
$F(000)$	920	992	992
reflections collected/unique	11598/4420 [R(int) = 0.0931]	10491/3843 [R(int) = 0.0824]	11928/3614 [R(int) = 0.0611]
data/restraints/parameters	4420/1/253	3843/1/254	3614/1/257
goodness of fit	0.699	1.069	0.773
R1 ($I > 2\sigma(I)$)	0.0507	0.0777	0.0362
wR2 ($I > 2\sigma(I)$)	0.0740	0.2321	0.0496
absolute structure parameter	0.02(2)	0.00(5)	0.01(3)

Table 2. Polymerization of Norbornene with 1/MMAO[a]

entry	NB (g)	solvent	T (°C)	Al/cat	yield (g)	conv. (%)	activity[b]	M_w (10^6 g/mol)[c]	PDI[c]
1	1.0	DCM	30	500	0.495	49.50	1.49	1.85	1.23
2	2.0	DCM	30	500	1.092	54.60	3.28	1.90	1.17
3	3.0	DCM	30	500	1.574	52.47	4.72	2.02	1.12
4[d]	2.0	DCM	30	500	0.975	48.75	2.92	2.00	1.13
5[e]	2.0	DCM	30	500	1.250	62.50	1.88	1.91	1.19
6[f]	2.0	DCM	30	500	1.379	68.95	0.83	1.83	1.20
7	2.0	DCM	30	100	0.353	17.65	1.06	1.93	1.17
8	2.0	DCM	30	1000	1.327	66.35	3.98	1.84	1.23
9	2.0	DCM	30	2000	1.368	68.40	4.10	1.70	1.31
10	2.0	1,2-DCE	30	500	1.820	91.00	5.46	1.77	1.27
11	1.0	1,2-DCE	0	500	0.453	45.30	1.36	-	-
12	1.0	1,2-DCE	30	500	0.637	63.70	1.91	-	-
13	1.0	1,2-DCE	50	500	0.656	65.60	1.97	-	-
14	1.0	1,2-DCE	70	500	0.610	61.00	1.83	-	-
15	2.0	PhCl	30	500	0.385	19.25	1.16	-	-
16	2.0	toluene	30	500	trace	-	-	-	-
17	2.0	CHCl$_3$	30	500	0.121	6.05	0.36	-	-

[a] Cat. 1 μmol; 2 min; V_{total} 25.0 mL. [b] 10^7 g of PNB/mol·h·atm. [c] Determined by GPC. [d] 1 min. [e] 4 min. [f] 10 min.

Scheme 2. Control Experiments

1) Ag(OTf) (5 equivalents)
or AgBF$_4$ (23.6 equivalents)
2) NBE, 30°C, 11h, 1.2-DCE → PNB
not observed

1) MMAO (Al/Ni: 500)
2) NBE, 30°C, 2 min., 1.2-DCE → PNB
up to 5.46 × 10^7 gPNB/mol cat. h
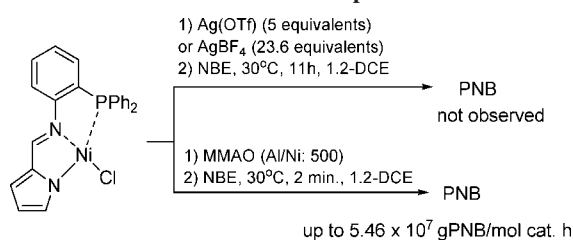
Table 3. Influence of Catalysts on the Activities[a]

entry	cat.	yield (g)	conv. (%)	activity[b]	M_w (10^6 g/mol)[c]	PDI[c]	TGA/°C
1	1	1.820	91.00	5.46	1.770	1.27	453.47
2	2	1.288	64.40	3.86	1.778	1.27	453.81
3	3	0.868	43.40	2.60	1.822	1.24	454.49
4	4	trace	-	-	-	-	-

[a] Cat., 1 μmol; Al/Cat. (mol), 500; NBE, 2.0 g; V_{total}, 25.00 mL; 30 °C; 2 min; 1,2-DCE. [b] 10^7 g of PNB/mol·h; [c] Determined by GPC.

= 0.71073 Å) radiation. An empirical absorption correction was applied using the SADABS program.[11] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations on F2 using the SHELXTL program package (PC version).[12] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinements were given in Table 1. Further details were included in the Supporting Information.

Synthesis of Ligand L1. In the presence of silicon–aluminum 135 and 4 Å molecular sieves, pyrrole-2-carboxaldehyde (1.78 g,

(11) Sheldrick, G. M. *SADABS: Program for Empirical Absorption Correction Of Area Detector Data*; University of Göttingen: Göttingen, Germany, 1996.

(12) *SHELXTL V 5.03 Program Package*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1995.

18.7 mmol) was treated with 2-(diphenylphosphino)aniline (4.71 g, 17.0 mmol) in toluene (60 mL). The solution was heated to 80 °C and stirred for 26 h. Then the insoluble matters were eliminated by celite filtration, and the filtrate was concentrated under reduced pressure. The residue was purified by recrystallization from ethanol, and the white crystals were collected. Yield: 4.81 g (80%). ^{1}H NMR (CDCl$_3$/TMS, 300 MHz): δ = 9.18 (brs, 1 H, NH), 8.00 (s, 1 H, CH=N), 7.37–7.23 (m, 11 H), 7.10–7.01 (m, 2 H), 6.77–6.82 (m, 2 H), 6.49–6.51 (m, 1 H), 6.18–6.20 (m, 1 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 153.8 (d, J = 18.0 Hz), 148.5, 148.4, 137.1 (d, J = 10.0 Hz), 134.0 (d, J = 20 Hz), 132.7, 132.6, 132.5, 130.8, 129.8, 128.4, 128.3, 128.2, 125.4, 122.9, 117.1, 117.0, 115.9, 110.1. ^{31}P NMR: -12.8. IR (KBr): $\nu_{C=N}$ 1619 cm^{-1}. MS (EI, m/z): 44 (100), 354 (M+, 53), 183 (43), 277 (40), 353 (31), 261 (26), 41 (12), 199 (12). Anal. Calcd. for $C_{23}H_{19}N_2P$: C, 77.95; H, 5.40; N, 7.90. Found: C, 78.19; H, 5.58; N, 7.80.

Synthesis of Complex 1. To a mixture of anhydrous $NiCl_2$ (0.726 g, 2.05 mmol) and ligand **L1** (0.253 g, 1.95 mmol) was added anhydrous ethanol (25 mL). The solution was stirred and refluxed for 18 h and then was cooled to room temperature. The dark-red precipitate was collected, washed with anhydrous ethanol, dissolved in CH_2Cl_2, and filtrated. The filtrate was concentrated under reduced pressure. The residue was purified by recrystallization from CH_2Cl_2 to give a dark-red solid. Yield: 0.546 g (63.0%). The other complexes **2−4** were synthesized via the same procedure.

1: ^1H NMR (DMSO-d_6, 300 MHz): δ = 8.53 (s, 1 H), 7.82–7.89 (m, 5 H), 7.49–7.64 (m, 8 H), 7.20–7.26 (m, 1 H), 6.94 –6.97 (m, 2 H), 6.26–6.27 (m, 1 H). ^{31}P NMR (CDCl$_3$, 121 MHz): 27.6. Anal. Calcd. for $C_{23}H_{18}ClN_2NiP$: C, 61.37; H, 4.05; N, 6.26; Cl, 7.92. Found: C, 61.79; H, 4.37; N, 6.60; Cl, 7.81. IR (KBr): $\nu_{C=N}$ 1552 cm^{-1}. MS (EI, *m/z*): 447 ((M+1)$^+$,18), 210 (100), 282 (29), 351 (15). X-ray: Crystal suitable for X-ray analysis grows from CH_2Cl_2−pentane.

2: yield, 41.3%. ^1H NMR (CDCl$_3$/TMS, 300 MHz): δ = 7.85–7.92 (m, 5 H), 7.40–7.54 (m, 9 H), 7.26–7.30 (m, 1 H), 7.09–7.13 (m, 1 H), 6.97–7.00 (m, 1 H), 6.31–6.33 (m, 1 H). ^{31}P NMR: 32.5. Anal. Calcd. for $C_{23}H_{18}BrN_2NiP$: C, 56.15; H, 3.69; N, 5.69; Br, 16.24. Found: C, 55.51; H, 3.66; N, 4.96; Br, 16.34. IR (KBr): $\nu_{C=N}$ 1552 cm^{-1}. MS (EI, *m/z*): 490 (M$^+$, 50), 57 (100), 97 (80), 492 (70), 411 (36), 349 (34). X-ray: Crystal suitable for X-ray analysis grows from CH_2Cl_2.

3: yield, 70.5%. ^1H NMR (CDCl$_3$/TMS, 300 MHz): δ 8.05 (d, 2.1 Hz, 1 H), 7.84–7.92 (m, 4 H), 7.70 (s, 1 H), 7.42–7.54 (m, 8 H), 7.19–7.27 (m, 1 H), 7.08–7.14 (m, 1 H), 7.00 –7.02 (m, 1 H), 6.28–6.31 (m, 1 H). ^{31}P NMR: 41.8. Anal. Calcd. for $C_{23}H_{18}IN_2NiP$: C, 51.25; H, 3.37; N, 5.20; I, 23.55. Found: C, 50.88; H, 4.06; N, 4.58; I, 23.25. IR (KBr): $\nu_{C=N}$ 1551 cm^{-1}. MS (EI, *m/z*): 538 (M+, 63), 411 (100), 413 (42), 183 (38), 540 (28), 539 (18).

4: yield, 80.6%. ^1H NMR (CDCl$_3$/TMS, 300 MHz): 8.17 (s, 1 H, CH=N), δ = 7.79–7.86 (m, 4 H), 7.39–7.64 (m, 10 H), 7.20–7.27 (m, 1 H), 7.06–7.09 (m, 1 H), 6.40 –6.42 (m, 1 H). ^{31}P NMR: 42.3. Anal. Calcd. for $C_{23}H_{18}ClN_2PdP$: C, 55.78; H, 3.66; N, 5.66. Found: C, 55.34; H, 3.48; N, 5.4. IR (KBr): $\nu_{C=N}$ 1547 cm^{-1}. MS (EI, *m/z*): 494 (M+, 30), 183 (100), 496 (28), 275 (27), 459 (5), 353 (18). X-ray: Crystal suitable for X-ray analysis grows from CH_2Cl_2−Hexane.

General Procedure for Polymerization of Norbornene. To a solution of norbornene and precatalyst (1 μmol) in CH_2Cl_2 was added MMAO (1.9 M in toluene) via a syringe. After the desired time, the reaction mixture was quenched by adding acidified EtOH (5 mL, EtOH/concentrated HCl, 10/1, v/v). The mixture was poured into a solution of concentrated HCl in EtOH (5%, v/v) and stirred for 12 h. The polymer was collected by filtration, washed with EtOH, and dried under reduced pressure at 50 °C to constant weight.

Typical IR spectra for the obtained PNB (KBr): 2946 (vs), 2867 (vs), 1474 (s), 1453 (s), 1375 (m), 1294 (m), 1257 (m), 1223 (m), 1146 (m), 1107 (m), 890 (m). ^1H NMR (*o*-dichlorobenzene-d_4, 300 MHz, 110 °C): δ 0.90–2.70 (m). ^{13}C NMR (*o*-dichlorobenzene-d_4, 75 MHz, 110 °C): δ 29.70–32.05 (m), δ 35.34–39.88 (m), δ 47.05–49.24 (m).

Supporting Information Available: NMR spectra of **LI**, complexes **1−4**, and polymer as well as X-ray crystallographic data in CIF format for **1**, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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