# Influence of Backbone Substituents on the Ethylene (Co)polymerization Properties of α-diimine Pd(II) and Ni(II) Catalysts

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S *Supporting Information*

ABSTRACT: A series of α-diimine ligands with different substituents on the acenaphthyl backbone were synthesized and characterized. The corresponding Ni(II) and Pd(II) complexes were prepared and used in ethylene polymerization and copolymerization with methyl acrylate. In ethylene polymerization, these Ni(II) complexes showed activities of up to 1.6×10^7 g/((mol of Ni) h), generating polyethylene with a molecular weight (M_n) of up to 4.2×10^5. Interestingly, these Ni(II) complexes behave very similarly in ethylene polymerization except for the complex with two methoxy substituents on the *ortho* position of the acenaphthyl backbone, in which case about 3 times higher polyethylene molecular weight and much lower branching density were observed. The ligand substituent effect is much more dramatic for the Pd(II) complexes. In ethylene polymerization, activities of up to 1.7×10^5 g/((mol of Pd) h) and a polyethylene molecular weight (M_n) of up to 4.7×10^4 could be obtained. The Pd(II) complex with two methoxy substituents on the ortho position of the acenaphthyl backbone demonstrated much higher activity and generated polyethylene with about 3 times higher molecular weight than that for the classic Pd(II) complex. A similar trend was maintained in ethylene−methyl acrylate copolymerization.
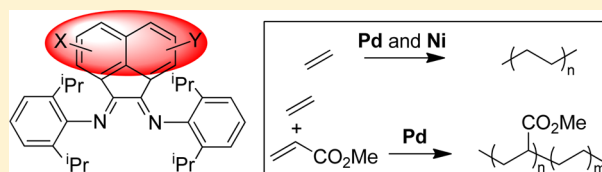
INTRODUCTION

Late-transition-metal catalysts have received intense attention due to their great functional group tolerance and their potential applications in olefin−polar vinyl monomer copolymerization.[1] In the 1990s, Brookhart et al. demonstrated that Ni(II) and Pd(II) complexes bearing sterically bulky α-diimine ligands can efficiently catalyze olefin polymerization and copolymerization with acrylate or vinyl ketone monomers.[2] The polymer microstructures and topologies (linear, hyperbranched, and dendritic) can be controlled via polymerization conditions using these catalysts.[3] Since then, great successes have been achieved in the synthesis of various polymers and copolymers with structures that have not been accessible previously.[4,5] A major research direction in this field is the modification of α-diimine ligand structures to obtain high-performance catalysts (Chart 1, **I**).

The ortho aryl substituents are positioned at the metal axial positions, making them capable of blocking monomer access and suppress the associative chain transfer process. For example, Rieger et al. showed that Ni(II) catalysts bearing meta-substituted terphenyl-based α-diimine ligands possess high activity and stability in ethylene polymerization (Chart 1, **II**).[6] Guan et al. designed some cyclophane-based α-diimine Ni(II) and Pd(II) catalysts, which showed greatly enhanced thermal stability in ethylene polymerization and copolymerization reactions.[7] The Brookhart, Daugulis, and Coates group studied the ethylene and olefin polymerization properties of some Ni(II) and Pd(II) catalysts bearing a sandwich structured α-diimine ligand (Chart 1, **III**).[8] Recently, Long et al. reported some α-diimine Ni(II) catalysts bearing dibenzhydryl moiety with high

stability and high activity in ethylene polymerization (Chart 1, **IV**).[9] Our group further showed that Pd(II) catalysts with similar ligands can afford semicrystalline polymers and copolymers in ethylene polymerization and copolymerization with methyl acrylate.[9e] In addition to ligand steric modifications, the Guan group and our group demonstrated that α-diimine ligand electronic effects can dramatically influence the catalytic properties of the palladium catalysts (Chart 1, **V**).[10]

Another effective strategy is modification on the α-diimine ligand backbone. For example, Wu et al. investigated a series of α-diimine Ni(II) and Pd(II) catalysts with various backbone structures including camphyl, phenyl, 4-fluorophenyl, and 4-methylphenyl (Chart 1, **VI**).[11] Brookhart et al. showed that the α-diimine Ni(II) catalysts with alkyl backbones generated polymers with higher molecular weight and narrower polydispersity in comparison to those with a planar acenaphthyl backbone (Chart 1, **VII**).[12] The planar acenaphthyl backbone has been widely used in the synthesis of various α-diimine ligand structures. Despite so many years of research on the ligand backbone modifications, there have been no studies concerning the influence of acenaphthyl backbone substituents on the catalyst properties. In this contribution, we describe the synthesis and characterization of a series of Ni(II) and Pd(II) complexes with different substituents on the acenaphthyl backbone. Furthermore, their performance in ethylene polymerization and copolymerization reactions was investigated.

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Chart 1. Different α-Diimine Ligand Structures
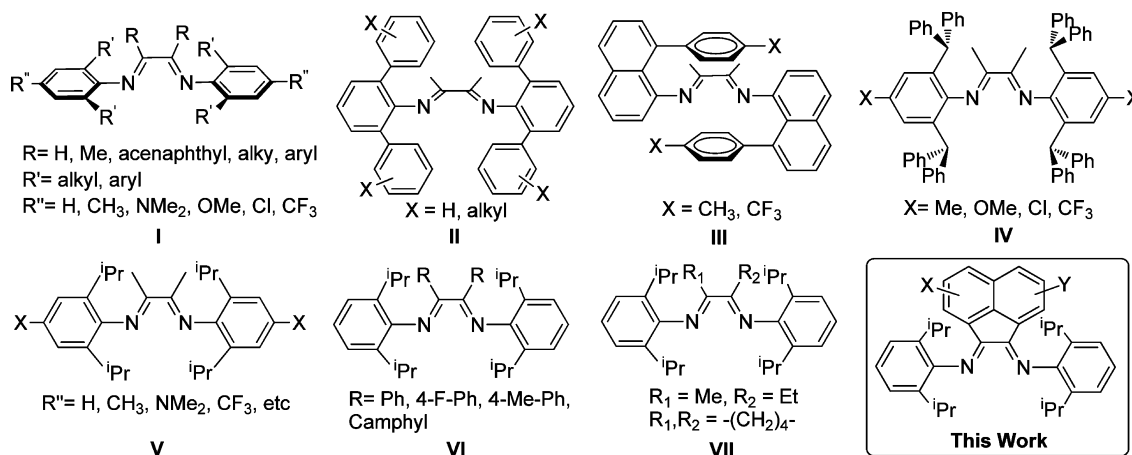
Scheme 1. Synthesis of the Ni complexes Ni-1−Ni-6 and the Pd Complexes Pd-1−Pd-6
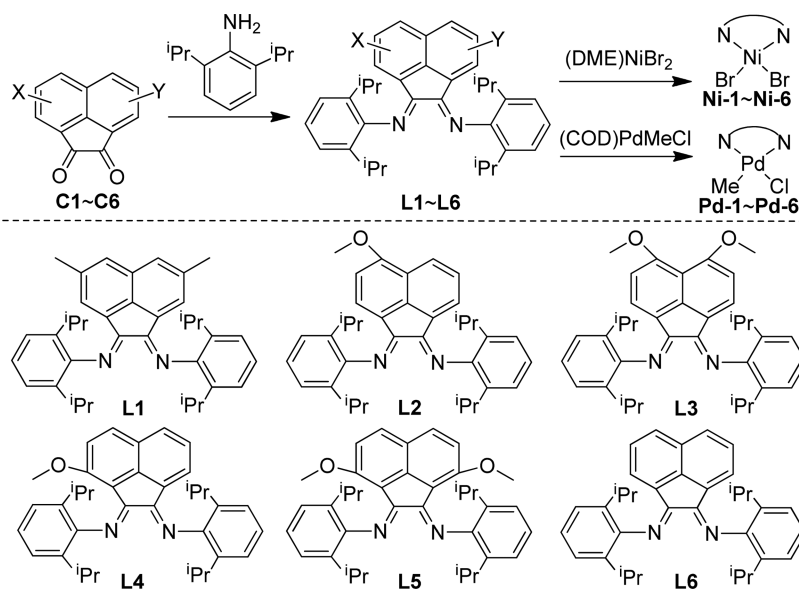
RESULTS AND DISCUSSION

Synthesis and Characterization of the Ni Complexes Ni-1−Ni-6 and the Pd Complexes Pd-1−Pd-6. The substituted acenaphthenequinone ligands **C1−C5** were prepared using modified literature procedures.[13−17] Interestingly, these substituted acenaphthenequinone ligands have not been used to prepare α-diimine ligands. The α-diimine ligands **L1−L5** were obtained in 60−70% yields from the reaction of **C1−C5** with ca. 2 equiv of 2,6-diisopropylaniline. The reaction of these ligands with 1 equiv of (DME)NiBr$_2$ (DME = ethylene glycol dimethyl ether) led to the formation of the Ni complexes **Ni-1−Ni-5** in 75−85% yields (Scheme 1). The Ni complexes were characterized using elemental analysis and mass spectrometry. The reaction of these ligands with 1 equiv of (COD)PdMeCl (COD = 1,5-cyclooctadiene) led to the formation of the Pd complexes **Pd-1−Pd-5** in 75−85% yields. The Pd complexes were characterized by ^{1}H NMR, ^{13}C NMR, and elemental analysis. The classic ligand **L6**, nickel complex **Ni-6**, and palladium complex **Pd-6** were prepared for comparison.

The molecular structures of **Ni-1**, **Ni-5**, **Pd-1**, and **Pd-5** were determined by X-ray diffraction analysis (Figures 1 and 2). The geometry at the Ni center is distorted tetrahedral. The geometry at the Pd center is square planar. The bond distances and bond angles are typical in comparison with previously reported α-diimine Ni(II) and Pd(II) complexes. Complex **Ni-1** exists as a dimeric form in the solid state, while complex **Ni-5** exists as a monomeric form in the solid state. The average dihedral angles between the Ni−N−N plane and the aniline phenyl plane are 83.7° for complex **Ni-1** and 74.1° for complex **Ni-5**. These results suggest that the o-MeO substituents on the acenaphthyl backbone indeed influence the steric environment of the metal center.

Ethylene Polymerization Studies Using the Nickel Complexes. All of the Ni(II) complexes **Ni-1−Ni-5** are highly active in ethylene polymerization when activated using methylaluminoxane (MAO), and the polymerization results are summarized in Table 1. Under our polymerization conditions, activities of up to 1.6×10^7 g/((mol of Ni) h) and polyethylene molecular weights (M_n) of up to 4.2×10^5 could be obtained. At 20 °C and under the same conditions, complexes **Ni-1−Ni-4** showed activity very similar to that of the classic complex **Ni-6** (Table 1, entries 1−4 and 6). In addition, they generated polyethylene with similar molecular weights, melting temperatures, and branching densities. In contrast, complex **Ni-5**
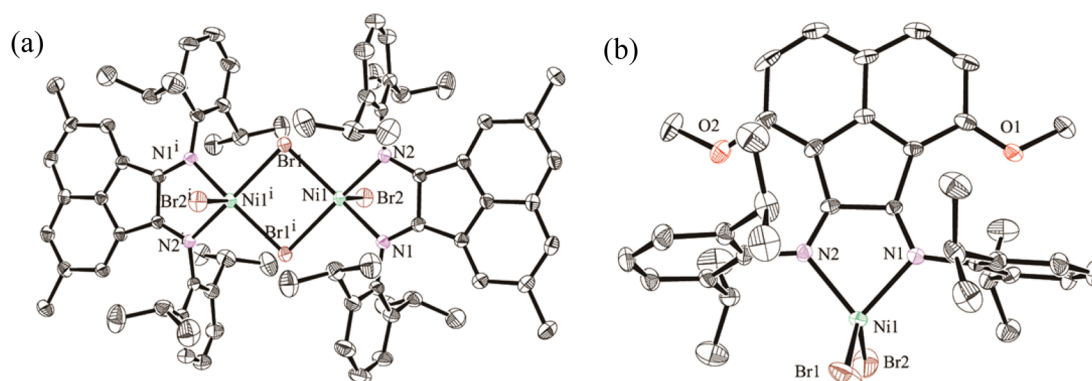
Figure 1. (a) Molecular structure of complex **Ni-1**. Selected bond lengths (Å) and angles (deg): Ni1−Br1 = 2.4498(7), Ni1−Br2 = 2.4037(7), Ni1−N1 = 2.094(2), Ni1−N2 = 2.125(2); Br1−Ni1−Br2 = 104.98(3), N1−Ni1−N2 = 79.17(8). (b) Molecular structure of complex **Ni-5**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1−Br1 = 2.3383(18), Ni1−Br2 = 2.3420(18), Ni1−N1 = 2.024(6), Ni1−N2 = 2.029(7); Br1−Ni1−Br2 = 120.37(7), N1−Ni1−N2 = 81.7(3). Hydrogen atoms have been omitted for clarity. Atoms are drawn at the 30% probability level.
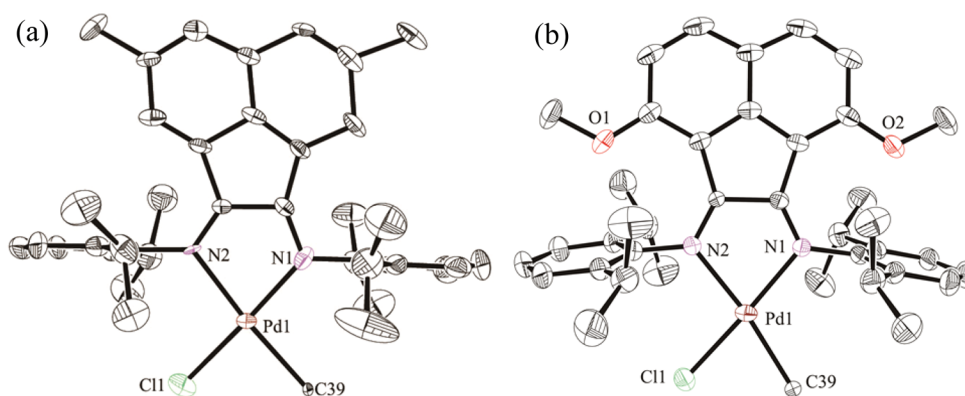

Figure 2. (a) Molecular structure of complex **Pd-1**. Selected bond lengths (Å) and angles (deg): Pd(1)−Cl(1) = 2.232(5), Pd(1)−C(39) = 2.236(9), Pd(1)−N(1) = 2.050(13), Pd(1)−N(2) = 2.163(8); N(1)−Pd(1)−N(2) = 78.99(19), N(2)−Pd(1)−Cl(1) = 98.7(3), N(1)−Pd(1)−C(39) = 96.3(4), C(39)−Pd(1)−Cl(1) = 86.08(15). (b) Molecular structure of complex **Pd-5**. Solvent molecules (CH₃Cl) are also omitted. Selected bond lengths (Å) and angles (deg): Pd(1)−Cl(1) = 2.214(3), Pd(1)−C(39) = 2.176(8), Pd(1)−N(1) = 2.102(3), Pd(1)−N(2) = 2.111(3); N(1)−Pd(1)−N(2) = 78.96(11), N(2)−Pd(1)−Cl(1) = 98.38(10), N(1)−Pd(1)−C(39) = 108.0(3), C(39)−Pd(1)−Cl(1) = 74.7(2). Hydrogen atoms have been omitted for clarity. Atoms are drawn at the 30% probability level.

showed lower activity, generating polyethylene with ca. 3 times higher molecular weight and much lower branching density (Table 1, entry 5).

At longer polymerization time (30 min) and 20 °C, the activity differences between **Ni-5** and **Ni-1**/**Ni-6** became smaller, while the polyethylene molecular weight differences were maintained (Table 1, entries 7−9). The thermal stability of complexes **Ni-5** and **Ni-6** at 40 °C was investigated (Table S1 in the Supporting Information). The polyethylene yield versus time curves (Figure S1 in the Supporting Information) clearly showed that the activity differences between complexes **Ni-5** and **Ni-6** became smaller at longer polymerization times. When the time was set at 60 min, the polyethylene yield of complex **Ni-5** was very close to that of complex **Ni-6**. These results suggested that complex **Ni-5** is thermally more stable than complex **Ni-6** under these conditions. The temperature dependence of complexes **Ni-1**, **Ni-5**, and **Ni-6** was also studied (Table 1, entries 10−18). For all three complexes, the activity and the polyethylene molecular weight decreased with increasing temperature. When Et₂AlCl or EtAlCl₂ was used as cocatalyst, slightly higher activity and lower polyethylene molecular weight were observed (Table 1, entries 19 and 20).

The polyethylene microstructures were analyzed by ¹³C NMR (Figures S30−S32 in the Supporting Information) according to the literature,[18] which showed that the polyethylene is highly branched. In addition, the branching densities determined using ¹³C NMR are very close to those determined by ¹H NMR (Table S5 in the Supporting Information). Although lower branching density was observed for complex **Ni-5**, the Me, Et, Pr, and long-chain branching distributions among complexes **Ni-1**, **Ni-5**, and **Ni-6** are very similar to each other (Table S5). The polyethylene generated using different nickel complexes showed dramatically different mechanical properties. The polyethylene generated from complex **Ni-1** showed slightly worse mechanical properties than that from the classic complex **Ni-6** in a stress versus strain analysis (Figure 3). In contrast, the polyethylene generated using complex **Ni-5** showed much better performance, with a strain at break of more than 550%. It was demonstrated previously that the molecular weights, branching densities, and branching topologies all contribute to the differences in the mechanical properties of the polyethylene materials.[19] In that study, high molecular weight was shown to be essential to achieve high tensile properties, while higher branching density does not necessarily led to better elastic properties. In our study, the very high molecular weight and the moderate branching density for

Table 1. Ethylene Polymerization with Nickel Complexes Ni-1−Ni-6[a]

entry	cat.	T (°C)	t (min)	yield (g)[b]	activity[b]	$M_n{}^c$ (×10^{-4})	PDI[c]	$T_m{}^d$ (°C)	B^e
1	Ni-1	20	10	2.65	15.9	8.8	2.50	58	81
2	Ni-2	20	10	2.34	14.0	8.7	2.14	60	82
3	Ni-3	20	10	2.70	16.2	8.2	2.18	49	91
4	Ni-4	20	10	2.35	14.1	11.2	2.00	60	80
5	Ni-5	20	10	1.08	6.5	28.4	1.96	68	52
6	Ni-6	20	10	2.88	15.4	8.0	2.80	61	79
7	Ni-1	20	30	3.42	6.8	14.2	1.94	61	85
8	Ni-5	20	30	1.82	3.6	41.8	2.01	75	56
9	Ni-6	20	30	3.62	7.2	13.8	1.89	67	84
10	Ni-1	40	10	2.31	13.9	5.9	2.65	f	94
11	Ni-1	60	10	2.10	12.6	5.4	2.19	f	100
12	Ni-1	80	10	1.63	9.8	4.3	2.38	f	102
13	Ni-5	40	10	0.86	5.2	17.5	2.28	f	88
14	Ni-5	60	10	0.74	4.4	10.8	2.34	f	107
15	Ni-5	80	10	0.72	4.3	6.3	2.41	f	108
16	Ni-6	40	10	2.34	14.0	4.9	2.81	f	95
17	Ni-6	60	10	2.0	12.0	3.9	2.69	f	101
18	Ni-6	80	10	1.23	7.4	3.4	2.66	f	101
19[g]	Ni-5	20	10	1.00	6.0	25.7	2.49	60	68
20[h]	Ni-5	20	10	0.82	4.9	21.0	2.81	59	66

[a]Conditions unless specified otherwise: 1 μmol of Ni, MAO cocatalyst, Al/Ni = 500, 1 mL of CH$_2$Cl$_2$, 49 mL of toluene, 9 atm. [b]Activity = 10^6 g/((mol of Ni) h). The yields and activities are the average of at least two runs. [c]Molecular weight was determined by GPC in o-dichlorobenzene at 140 °C using polystyrene standards. [d]Determined by differential scanning calorimetry, second heating. [e]B = branches per 1000 carbons, determined by ^{1}H NMR spectroscopy. [f]T_m less than 25 °C. [g]Cocatalyst Et$_2$AlCl. [h]Cocatalyst EtAlCl$_2$.
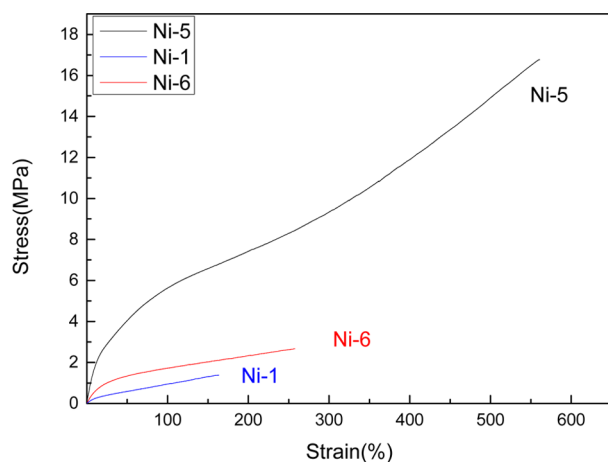

Figure 3. Stress versus strain for polyethylene generated using complexes **Ni-1**, **Ni-5**, and **Ni-6** at 20 °C and 30 min (Table 1, entries 7−9).

the polyethylene generated by complex **Ni-5** might be the key to its superior mechanical properties.

Ethylene Polymerization Studies Using the Palladium Complexes. All of these palladium complexes are active in ethylene polymerization when activated using 1.2 equiv of tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBAF). In addition, these palladium complexes are more sensitive to the backbone substitution in ethylene polymerization in comparison with the nickel complexes (Table 2). Under our polymerization conditions, activities of up to 1.7 × 10^5 g/((mol of Pd) h) and polyethylene molecular weights (M_n) of up to 4.7 × 10^4 could be obtained. Complexes **Pd-5** and **Pd-3** showed activities much higher than those of the rest of the palladium complexes (Table 2, entries 1−6). Specifically for complex **Pd-5**, ca. 3 times higher polyethylene molecular weight was observed in comparison with the classic complex **Pd-6**. Complexes **Pd-1**, **Pd-5**, and **Pd-6** were selected for temperature dependence

Table 2. Ethylene Polymerization with Palladium Complexes Pd-1−Pd-6[a]

entry	cat.	T (°C)	yield (g)[b]	activity[b]	$M_n{}^c$ (10^{-3})	PDI[c]	B^d
1	Pd-1	20	0.22	2.2	21.0	1.43	107
2	Pd-2	20	0.23	2.3	18.1	1.38	106
3	Pd-3	20	0.35	3.5	23.6	1.46	110
4	Pd-4	20	0.28	2.8	14.0	1.53	107
5	Pd-5	20	0.51	5.1	36.0	1.16	111
6	Pd-6	20	0.27	2.7	13.0	1.42	110
7	Pd-1	40	0.96	9.6	25.9	1.52	112
8	Pd-1	60	0.21	2.1	10.2	1.87	108
9	Pd-1	80	0.11	1.1	5.1	2.32	117
10	Pd-5	40	1.73	17.3	47.2	1.24	101
11	Pd-5	60	0.69	6.9	20.6	1.89	104
12	Pd-5	80	0.15	1.5	6.2	2.74	104
13	Pd-6	40	1.31	13.1	18.2	1.57	108
14	Pd-6	60	0.35	3.5	9.0	1.99	109
15	Pd-6	80	0.1	1.0	4.8	2.45	117

[a]Conditions: 10 μmol of precatalyst, 1.2 equiv of NaBAF, 2 mL of CH$_2$Cl$_2$, 48 mL of toluene, 9 atm, 1 h. [b]Activity = 10^4 g/((mol of Pd) h). Yield and activity are average of at least two runs. [c]Molecular weight was determined by GPC using polystyrene standards. [d]B = branches per 1000 carbons, determined by ^{1}H NMR spectroscopy.

studies (Table 2, entries 7−15). The activity reached a maximum at 40 °C and decreased afterward. The polyethylene molecular weight decreased with increasing polymerization temperature. The polyethylene branching density is relatively insensitive to the ligand structures or the polymerization temperatures.

Ethylene−Methyl Acrylate (E-MA) Copolymerization Studies Using the Palladium Complexes. The performance of these palladium complexes in ethylene−MA copolymerization was also studied (Table 3). These complexes incorporated MA comonomer on a very similar level except for complex **Pd-4** (Table 3, entries 1−18). The relatively lower MA incorporation

Table 3. Copolymerization of Ethylene and MA with Palladium Complexes Pd-1−Pd-6[a]

entry	cat.	[MA] (M)	yield (g)[b]	activity[b]	X_{MA}[c] (%)	M_n[d] (×10⁻³)	PDI	B[e]
1	**Pd-1**		1.7	3.78		18.1	1.61	114
2	**Pd-1**	1	0.27	0.6	4.4	9.8	1.71	116
3	**Pd-1**	2	0.19	0.42	7.1	6.1	1.57	111
4	**Pd-2**		1.96	4.36		19.1	1.62	110
5	**Pd-2**	1	0.44	0.97	3.5	7.2	1.71	111
6	**Pd-2**	2	0.26	0.58	6.2	5.4	1.54	112
7	**Pd-3**		2.16	4.8		44.0	1.60	110
8	**Pd-3**	1	0.40	0.89	4.9	17.0	1.74	111
9	**Pd-3**	2	0.25	0.56	7.9	12.3	1.70	112
10	**Pd-4**		2.14	4.76		29.3	1.84	106
11	**Pd-4**	1	1.5	3.33	1.9	19.0	1.63	108
12	**Pd-4**	2	0.74	1.64	4.1	13.2	1.66	104
13	**Pd-5**		2.08	4.62		46.5	1.74	104
14	**Pd-5**	1	0.62	1.38	4.1	18.5	1.68	102
15	**Pd-5**	2	0.45	1.0	7.0	13.3	1.70	103
16	**Pd-6**		1.7	3.78		12.1	1.69	112
17	**Pd-6**	1	0.3	0.67	4.3	8.0	1.58	110
18	**Pd-6**	2	0.2	0.44	7.2	5.7	1.76	115

[a]Conditions: 0.030 mmol of precatalyst, 1.2 equiv of NaBAF, total volume of DCM and MA 25 mL, 30 °C, 1 atm, 15 h. [b]Activity = 10³ g/((mol of Pd) h). Yield and activity are average of at least two runs. [c]X_{MA}= MA incorporated (mol %). [d]Molecular weight was determined by GPC calibration using polystyrene standards. [e]B = branches per 1000 carbons, branching numbers were determined using ¹H NMR spectroscopy. The branches ending with functional groups were added to the total branches.

of complex **Pd-4** is not fully understood and is currently under investigation. With higher MA concentration, higher MA incorporation, lower activity, and lower copolymer molecular weight were observed. Similarly to ethylene homopolymerization, much higher copolymer molecular weight was observed for complexes **Pd-3** and **Pd-5** versus the classic complex **Pd-6**. The copolymer branching density is insensitive to the ligand structures or the polymerization conditions.

In α-diimine Ni(II) and Pd(II) catalyzed olefin polymerization and copolymerization, higher steric bulkiness of the ligand structure usually leads to higher polymer molecular weight. Previously, the Guan group and our group showed that electronic perturbation of the α-diimine ligand showed very little effect in ethylene polymerization properties of the Ni(II) catalysts.[10] In α-diimine Pd(II) catalyzed ethylene polymerization and copolymerization, electron-donating substituents usually lead to higher polymer molecular weight. Ligand **L1** is very similar to the classic ligand **L6** both electronically and sterically. Therefore, the nickel and the palladium complexes based on ligand **L1** should behave similarly with the complex based on ligand **L6**. This is indeed what we observed in our studies. Ligand **L5** is electronically more donating and sterically more crowded than ligand **L6**. This is probably the major reason complexes **Ni-5** and **Pd-5** generated polyethylene and E-MA copolymer with much higher molecular weight than the classic complexes **Ni-6** and **Pd-6**. Ligands **L2−L4** should possess similar steric bulkiness and higher electron donating ability in comparison with the class ligand **L6**. This could explain the similar behavior in ethylene polymerization for complexes **Ni-2−Ni-4** and **Ni-6**. The higher polymer and copolymer molecular weight for complexes **Pd-2−Pd-4** versus **Pd-6** probably originates from electronic effects.

CONCLUSIONS

To conclude, we described the synthesis and polymerization studies of a series of α-diimine Ni(II) and Pd(II) complexes bearing different substituents on the acenaphthyl backbone. Very little difference was observed for the Ni(II) complexes in ethylene polymerization, except for the sterically bulky complex **Ni-5**. **Ni-5** generated polyethylene with much higher molecular weight and much lower branching density than the classic complex **Ni-6** and the rest of the nickel complexes. In contrast, the backbone substituents have some dramatic effects on the Pd(II)-catalyzed ethylene polymerization and copolymerization with methyl acrylate. Again, the sterically bulky complex **Pd-5** generated polyethylene and copolymer with much higher molecular weight than the classic complex **Pd-6**. This provides an alternative strategy to modify the ligand structures in the α-diimine framework and correspondingly influence the polymerization and copolymerization processes.

EXPERIMENTAL SECTION

General Considerations. All experiments were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Deuterated solvents used for NMR were dried and distilled prior to use. ¹H and ¹³C NMR spectra were recorded by a Bruker Ascend Tm 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ¹H and ¹³C NMR spectra were referenced to the residual solvent; coupling constants are given in Hz. Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China. X-ray diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The molecular weight and molecular weight distribution of the polymer, which is synthesized by complexes **Ni-1−Ni-6**, were determined by gel permeation chromatography (GPC) with a PL 210 instrument equipped with one Shodex AT-803S and two Shodex AT-806MS columns at 150 °C using trichlorobenzene as a solvent and calibrated with polystyrene standards. The molecular weight and the molecular weight distribution of the polymer synthesized by complexes **Pd-1−Pd-6** were determined by a gel permeation chromatograph (GPC) equipped with two linear Styragel columns (HR2 and HR4) at 40 °C using THF as a solvent and calibrated with polystyrene standards, and THF was employed as the eluent at a flow rate of 1.0 mL/min. Stress/strain experiments were performed at 10 m/min by means of a Universal Test Machine (UTM2502) at room temperature. Polymers were melt-pressed at 30−35 °C above their melting point to obtain the test specimens. The test specimens had 28 mm gauge length, 3 mm width, and

a thickness of 1 mm. At least five specimens of each copolymer were tested. A 1:4 mixture of the isomers 3,8-dimethylacenaphthenequinone and 4,7-dimethylacenaphthenequinone (**C1**),[13] 5-methoxyacenaphthenequinone (**C2**),[14] 5,6-dimethoxyacenaphthenequinone (**C3**),[15] 3-methoxy-acenaphthenequinone (**C4**),[16] 3,8-dimethoxyacenaphthenequinone (**C5**),[17] **L6**,[20] **Ni-6**, and **Pd-6** were prepared according to literature procedures.[2,10b]

Modifiied Procedure for the Preparation of 1,8-Dihydrox-ynaphthalene and 1,8-Dimethoxynaphthalene. A 250 mL round-bottom flask was charged with 16.9 g (320.3 mmol) of KOH and a magnetic stirring bar. The flask was heated with an electric jacket until the KOH melted (between 200 and 230 °C). Under a nitrogen atmosphere, 5 g (24.2 mmol) of 1,8-naphthalenesultone was added in small portions so that mixing was thorough. When 1,8-naphthalene-sultone was added, SO_2 was liberated from the flask. After the addition was finished, the mixture was stirred for another 15 min. The mixture was cooled to room temperature, and 40 mL of 0 °C concentrated HCl and 50 mL ethyl acetate were added. The aqueous layer was extracted with ethyl acetate (2×50 mL). The organic layer was dried with $MgSO_4$ and concentrated to give a black viscous oil, which was purified by column chromatography using EtOAc/PE (1/3) as an eluent to give 1,8-dihydroxynaphthalene as a white solid. Yield: 2.3 g, (60%). $R_f = 0.50$ (ethyl acetate/petroleum ether, 1/3). The ^1H NMR, ^{13}C NMR, and MS data agree well with literature reports.[21] To a solution of 1,8-dihydroxy-naphthalene (2.00 g, 12.5 mmol) in acetone (40 mL) were added K_2CO_3 (8.60 g, 62.5 mmol) and methyl iodide (7.09 g, 3.11 mL, 50 mmol). The reaction mixture was refluxed for 24 h. The progress of the reaction was monitored by thin-layer chromatography. At the end of the reaction, the solution was acidified with dilute HCl (2 mol/L, 50 mL) and extracted with CH_2Cl_2 (2×50 mL). The combined organic phases were washed with water and saturated NaCl, dried over $MgSO_4$, and concentrated under vacuum. A light brown crystalline solid corresponding to 1,8-dimethoxynaphthalene was obtained in quantitative yield. The ^1H NMR, ^{13}C NMR, and MS data agree well with literature reports.[21]

Bis[*N,N′*-(2,6-diisopropylphenyl)imino]-4,7-dimethylace-naphthene (L1). A solution of 2,6-diisopropylaniline (8.8 mmol), a 1:4 mixture of isomers 3,8-dimethylacenaphthenequinone and 4,7-dimethylacenaphthenequinone (4 mmol), and formic acid (0.1 mL) in ethanol (25 mL) were stirred at room temperature overnight. The compound 3,8-dimethylacenaphthenequinone remained unreacted at the end of the reaction and could be washed away with hot ethanol. The product was collected via filtration and washed with hot ethanol (3×20 mL). The resulting bright yellow solid was collected and dried under high vacuum. Yield: 60% based on 4,7-dimethylacenaphthene-quinone (1.02 g). $R_f = 0.50$ (petroleum ether/dcm, 1/2). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.55 (s, 2H, aryl-*H*), 7.34−7.16 (m, 6H, aryl-*H*), 6.48 (s, 2H, aryl-*H*), 3.19−2.87 (dt, 4H, C*H*Me$_2$), 2.3 (s, 6H, aryl-*Me*), 1.4−0.8 (dd, 24H, CH*Me$_2$*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.48 (N=C), 147.66, 138.25, 138.09, 135.56, 131.32, 129.46, 127.29, 124.48, 124.33, 123.44, 28.66, 23.53, 23.24, 22.46 (aryl-*Me*). Anal. Calcd for $C_{38}H_{44}N_2$: C, 86.31; H, 8.39; N, 5.30. Found: C, 86.02; H, 8.19; N, 5.36. HRMS (*m/z*): calcd for $C_{38}H_{45}N_2$ 529.3583, found 529.3572 [M + H]$^+$.

Bis[*N,N′*-(2,6-diisopropylphenyl)imino]-5-methoxyacenaph-thene (L2). A solution of 2,6-diisopropylaniline (5.5 mmol), 5-methoxy-acenaphthenequinone (2.5 mmol), and formic acid (0.1 mL) in methanol (25 mL) was stirred at room temperature overnight. The orange product was collected via filtration and washed with methanol (3×10 mL). The orange solid was collected and dried under high vacuum. Yield: 65% (0.86 g). $R_f = 0.40$ (ethyl acetate/petroleum ether, 1/20). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.09 (d, $J = 8.3$ Hz, 1H, aryl-*H*), 7.44−7.23 (m, 6H, aryl-*H*), 7.23 (s, 1H, aryl-*H*), 6.77−6.52 (m, 3H, aryl-*H*), 3.97 (s, 3H, aryl-O*Me*), 3.20−2.73 (m, 4H, C*H*Me$_2$), 1.38−0.84 (m, 24H, CH*Me$_2$*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.80 (N=C), 160.40 (N=C), 157.54 (O−C^{aryl}), 135.92, 126.97, 125.16, 124.37, 124.31, 124.12, 124.03, 123.54, 123.50, 123.15, 105.79, 55.96 (OMe), 28.70, 28.65, 23.63, 23.54, 23.31, 23.25. Anal. Calcd for $C_{37}H_{42}N_2O$: C, 83.73; H, 7.98; N, 5.28. Found: C, 83.45; H, 7.78; N, 5.31. HRMS (*m/z*): calcd for $C_{37}H_{43}N_2O$ 531.3375, found 531.3368 [M + H]$^+$.

Bis[*N,N′*-(2,6-diisopropylphenyl)imino]-5,6-dimethoxyace-naphthene (L3). A solution of 2,6-diisopropylaniline (5.5 mmol), 5,6-dimethoxyacenaphthenequinone (2.5 mmol), and formic acid (0.1 mL) in methanol (25 mL) was stirred at room temperature overnight. The product was collected via filtration and washed with methanol (3×10 mL). Then the orange solid was collected and dried under high vacuum. Yield: 60% (0.84 g). $R_f = 0.30$ (ethyl acetate/petroleum ether, 1/20). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.21 (dt, $J = 18.7$, 8.7 Hz, 6H, aryl-*H*), 6.58 (q, $J = 8.2$ Hz, aryl-*H*), 3.9 (s, 6H, aryl-O*Me*), 2.98 (dt, $J = 13.6$, 6.8 Hz, 4H, C*H*Me$_2$), 1.11 (dd, 24H, CH*Me$_2$*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.77 (N=C), 159.07 (O−C^{aryl}), 147.88, 145.53, 135.82, 125.80, 124.37, 123.97, 123.43, 122.24, 114.66, 106.52, 56.33 (OMe), 28.60, 23.61, 23.29. Anal. Calcd for $C_{38}H_{44}N_2O_2$: C, 81.39; H, 7.91; N, 5.00. Found: C, 81.08; H, 7.66; N, 4.96. HRMS (*m/z*): calcd for $C_{38}H_{45}N_2O_2$ 561.3481, found 561.3463 [M + H]$^+$.

Bis[*N,N′*-(2,6-diisopropylphenyl)imino]-3-methoxyacenaph-thene (L4). A solution of 2,6-diisopropylaniline (5.5 mmol), 3-methoxy-acenaphthenequinone (2.5 mmol), and formic acid (0.1 mL) in methanol (25 mL) was stirred at room temperature overnight. The orange product was collected via filtration and washed with methanol (3×10 mL). Then the orange solid was collected and dried under high vacuum. The solubility of **L4** is very poor in common organic solvents; therefore, only ^1H NMR data were collected. Yield: 65% (0.86 g). $R_f = 0.30$ (ethyl acetate/petroleum ether, 1/20). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, $J = 8.9$ Hz, 1H, aryl-*H*), 7.79 (d, $J = 8.2$ Hz, aryl-*H*), 7.23 (s, 1H, aryl-*H*), 7.05−7.23 (m, 6H, aryl-*H*), 7.06 (s, 1H, aryl-*H*), 6.57 (s, 1H, aryl-*H*), 4.19, 3.29 (s, 3H, aryl-O*Me*), 2.96 (td, 4H, C*H*Me$_2$), 1.21 (d, $J = 6.8$ Hz, 12H, CH*Me$_2$*), 0.97 (d, $J = 12.1$ Hz, 12H, CH*Me$_2$*). Anal. Calcd for $C_{37}H_{42}N_2O$: C, 83.73; H, 7.98; N, 5.28. Found: C, 83.51; H, 7.93; N, 5.37. HRMS (*m/z*): calcd for $C_{37}H_{43}N_2O$ 531.3375, found 531.3385 [M + H]$^+$.

Bis[*N,N′*-(2,6-diisopropylphenyl)imino]-3,8-dimethoxyace-naphthene (L5). 3,8-Dimethoxyacenaphthenequinone (2.5 mmol) in acetonitrile (50 mL) and acetic acid (20 mL) was heated under 90 °C reflux for 2 h. To this solution was added directly 2,6-diisopropylaniline (5.5 mmol), and the solution was heated under reflux for a further 72 h. The solution was evaporated under reduced pressure. The product was washed three times with 20 mL of hot ethanol. Then the bright orange solid was collected and dried under high vacuum. **L5** cannot be dissolved in common solvents; therefore, ^1H NMR or ^{13}C NMR data were not collected. Yield 75% (1.05 g). Anal. Calcd for $C_{38}H_{44}N_2O_2$: C, 81.39; H, 7.91; N, 5.00. Found: C, 81.20; H, 7.69; N, 5.19. HRMS (*m/z*): calcd for $C_{38}H_{45}N_2O_2$ 561.3481, found 561.3459 [M + H]$^+$.

Standard Procedure for the Synthesis of Complexes Ni-1−Ni-5. Complexes **Ni-1−Ni-5** were synthesized by the reaction of 1 equiv of (DME)NiBr$_2$ with the corresponding ligands in methylene chloride. The ligand (0.49 mmol) was added to 10 mL of methylene chloride in a Schlenk tube under a nitrogen atmosphere. A suspension of (DME)-NiBr$_2$ (0.49 mmol) in CH_2Cl_2 (10 mL) was added to the above solution. The resulting mixture was stirred at room temperature for 24 h. The solvent was evaporated under reduced pressure to afford a solid. The product was washed with 4×20 mL of diethyl ether and dried under vacuum.

(**$^{4,7\text{-diMe}}$N^N)NiBr$_2$ (Ni-1).** Yellow solid. Yield: 0.275 g, 75%. Anal. Calcd for $C_{38}H_{44}Br_2N_2Ni$: C, 61.08; H, 5.93; N, 3.75. Found: C, 61.28; H, 5.71; N, 3.46. MALDI-TOF-MS (*m/z*): 665.01 [M − Br]$^+$.

(**$^{5\text{-OMe}}$N^N)NiBr$_2$ (Ni-2).** Brown solid. Yield: 0.326 g, 85%. Anal. Calcd for $C_{37}H_{42}Br_2N_2NiO$: C, 59.31; H, 5.65; N, 3.74. Found: C, 59.53; H, 5.92; N, 3.48. MALDI-TOF-MS (*m/z*): 667.05 [M − Br]$^+$.

(**$^{5,6\text{-diOMe}}$N^N)NiBr$_2$ (Ni-3).** Brown solid. Yield: 0.326 g, 85%. Anal. Calcd for $C_{38}H_{44}Br_2N_2NiO_2$: C, 58.57; H, 5.69; N, 3.59. Found: C, 58.75; H, 5.73; N, 3.47. MALDI-TOF-MS (*m/z*): 697.09 [M − Br]$^+$.

(**$^{3\text{-OMe}}$N^N)NiBr$_2$ (Ni-4).** Brown solid. Yield: 0.326 g, 85%. Anal. Calcd for $C_{37}H_{42}Br_2N_2NiO$: C, 59.31; H, 5.65; N, 3.74. Found: C, 59.45; H, 5.81; N, 3.56. MALDI-TOF-MS (*m/z*): 667.07 [M − Br]$^+$.

(**$^{3,8\text{-diOMe}}$N^N)NiBr$_2$ (Ni-5).** Brown solid. Yield: 0.326 g, 85%. Anal. Calcd for $C_{38}H_{44}Br_2N_2NiO_2$: C, 58.57; H, 5.69; N, 3.59. Found: C, 58.85; H, 5.71; N, 3.36. MALDI-TOF-MS (*m/z*): 697.03 [M − Br]$^+$.

Standard Procedure for the Synthesis of Complexes Pd-1−Pd-5. Complexes **Pd-1−Pd-5** were synthesized by the reaction of

1 equiv of (COD)PdMeCl with the corresponding ligands in methylene chloride. The ligand (1 mmol) was added to 10 mL of methylene chloride in a Schlenk tube under a nitrogen atmosphere. A solution of (COD)PdMeCl (1 mmol) in CH_2Cl_2 (10 mL) was added to the above solution. The resulting mixture was stirred at room temperature for 24 h. The solvent was evaporated under reduced pressure to afford a solid. The product was washed with 4×20 mL of diethyl ether and dried under vacuum.

(^{4,7-di-Me}N^N)PdMeCl (**Pd-1**). Orange solid. Yield: 77% (528 mg). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.74 (d, J = 16.9 Hz, 2H, aryl-H), 7.54−7.27 (m, 6H, aryl-H), 6.37 (s, 1H, aryl-H), 6.14 (s, 1H, aryl-H), 3.50−3.31 (m, 4H, CHMe$_2$), 2.34 (s, 3H, Me), 2.33 (s, 3H, Me), 1.47 (d, J = 6.6 Hz, 6H, CHMe$_2$), 1.37 (d, J = 6.6 Hz, 6H, CHMe$_2$), 0.96 (d, J = 6.8 Hz, 6H, CHMe$_2$), 0.91 (d, J = 6.8 Hz, 6H, CHMe$_2$), 0.83 (s, 3H, Pd-Me). ^{13}C NMR (100 MHz, CDCl$_3$): δ 172.52 (N═C), 168.07 (N═C), 142.38, 141.54, 141.50, 139.51, 139.45, 139.25, 138.40, 131.52, 129.75, 129.26, 128.23, 127.38, 127.13, 126.43, 125.79, 125.57, 124.46, 123.72, 29.19 (Me), 28.71 (Me), 24.22, 23.85, 23.66, 23.40, 22.42, 22.41, 3.12 (Pd-Me). Anal. Calcd for C$_{39}$H$_{47}$ClN$_2$Pd: C, 68.31; H, 6.91; N, 4.09; Found: C, 68.11; H, 7.07; N, 4.28.

(^{5-OMe}N^N)PdMeCl (**Pd-2**). Orange solid. Yield: 75% (514 mg). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.23 (dd, J = 19.5, 8.3 Hz, 1H, aryl-H), δ 7.45 (dd, J = 15.5, 7.2 Hz, 1H, aryl-H), 7.40−7.28 (m, 6H, aryl-H), 6.72 (t, J = 7.7 Hz, 1H, aryl-H), 6.60 (d, J = 7.7 Hz, 1H, aryl-H), 6.39 (dd, J = 7.7, 3.8 Hz, 1H, aryl-H), 4.00 (d, J = 1.3 Hz, 3H, OMe), 3.61−3.25 (m, 4H, CHMe$_2$), 1.48 (d, J = 6.8 Hz, 6H, CHMe$_2$), 1.37 (d, J = 6.8 Hz, 6H, CHMe$_2$), 0.94 (ddd, J = 17.5, 9.6, 7.0 Hz, 12H, CHMe$_2$), 0.81 (s, 3H, Pd-Me). ^{13}C NMR (100 MHz, CDCl$_3$): δ 172.99 (N═C), 171.03 (N═C), 168.48 (N═C), 166.78 (N═C), 159.64, 159.19, 145.76, 142.54, 142.40, 141.60, 141.52, 139.85, 139.49, 138.72, 138.39, 128.24, 128.05, 127.82, 127.68, 127.32, 127.27, 127.14, 126.90, 126.70, 126.39, 126.01, 125.52, 125.31, 124.52, 124.49, 123.78, 123.54, 123.44, 119.84, 119.17, 107.07, 107.01, 56.49 (OMe), 56.44 (OMe), 29.20, 29.15, 28.72, 28.67, 24.31, 24.23, 23.93, 23.88, 23.75, 23.67, 23.46, 23.42, 2.90 (Pd-Me), 2.80 (Pd-Me). Anal. Calcd for C$_{38}$H$_{45}$ClN$_2$OPd: C, 66.37; H, 6.60; N, 4.07; Found: C, 66.58; H, 6.39; N, 4.12.

(^{5, 6-diOMe}N^N)PdMeCl (**Pd-3**). Orange solid. Yield: 71% (509 mg). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 7.52−7.23 (m, 6H, aryl-H), 6.70−6.59 (m, 2H, aryl-H), 6.51 (d, J = 8.2 Hz, 1H, aryl-H), 6.32 (d, J = 8.4 Hz, 1H, aryl-H), 3.92 (s, 6H, OMe), 3.39 (dtd, J = 20.8, 13.8, 6.9 Hz, 4H, CHMe$_2$), 1.41 (dd, J = 23.1, 6.7 Hz, 12H, CHMe$_2$), 0.96 (dd, J = 15.9, 6.9 Hz, 12H, CHMe$_2$), 0.60 (s, 3H, Pd-Me). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ 172.15 (N═C), 167.85 (N═C), 161.83, 161.40, 149.56, 143.03, 141.94, 140.15, 139.16, 128.24, 128.22, 127.74, 127.13, 124.73, 123.96, 119.35, 118.73, 115.31, 107.78, 107.71, 56.90 (OMe), 56.86 (OMe), 29.33, 28.93, 24.23, 23.83, 23.64, 23.47, 1.58 (Pd-Me). Anal. Calcd for C$_{39}$H$_{47}$ClN$_2$O$_2$Pd: C, 65.27; H, 6.60; N, 3.90; Found: C, 65.52; H, 6.43; N, 3.65.

(^{3-OMe}N^N)PdMeCl (**Pd-4**). Orange solid. Yield: 77% (528 mg). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 8.09 (dd, J = 17.3, 9.1 Hz, 1H, aryl-H), 7.95 (dd, J = 15.3, 8.0 Hz, 1H, aryl-H), 8.03−7.89 (m, 8H, aryl-H), 6.52, 6.32 (d, J = 7.3, 7.4 Hz, 1H, aryl-H), 3.45−3.21 (m, 4H, CHMe$_2$), 3.31 (d, J = 2.5 Hz, 3H, OMe), 1.47−1.32 (m, 12H, CHMe$_2$), 0.96 (ddd, J = 24.8, 12.3, 5.4 Hz, 12H, CHMe$_2$), 0.62, 0.45 (s, 3H, Pd-Me). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ 173.63 (N═C), 170.75 (N═C), 169.25 (N═C), 166.24 (N═C), 155.29, 155.22, 146.31, 145.56, 145.17, 143.00, 142.11, 140.24, 139.72, 139.29, 138.83, 126.21, 126.14, 125.99, 125.75, 125.63, 124.82, 124.01, 122.47, 121.80, 116.28, 111.60, 111.09, 57.28 (OMe), 57.01 (OMe), 29.50, 29.35, 29.16, 28.92, 24.20, 23.96, 23.81, 23.65, 23.56, 23.48, 23.44, 23.09, 4.11 (Pd-Me), 2.32 (Pd-Me). Anal. Calcd for C$_{38}$H$_{45}$ClN$_2$OPd: C, 66.37; H, 6.60; N, 4.07; Found: C, 66.54; H, 6.35; N, 3.97.

(^{3, 8-diOMe}N^N)PdMeCl (**Pd-5**). Orange solid. Yield: 69% (495 mg). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 7.97 (dd, J = 16.0, 9.0 Hz, 2H, aryl-H), 7.38−7.07 (m, 6H, aryl-H), 6.94 (t, J = 9.3 Hz, 2H, aryl-H), 3.35 (dt, J = 13.7, 6.8 Hz, 4H, CHMe$_2$), 3.25 (s, 6H, OMe), 1.42 (d, J = 6.7 Hz, 6H, CHMe$_2$), 1.38 (d, J = 6.7 Hz, 6H, CHMe$_2$), 0.99 (d, J = 2.0 Hz, 6H, CHMe$_2$), 0.98 (d, J = 2.0 Hz, 6H, CHMe$_2$), 0.34 (s, 3H, Pd-Me). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): δ 171.53 (N═C), 166.87 (N═C), 155.98, 155.92, 148.42, 146.00, 145.78, 140.16, 139.24, 134.96, 134.36,

126.70, 125.71, 122.36, 121.67, 121.37, 112.91, 112.87, 110.25, 109.79, 57.12 (OMe), 56.85 (OMe), 29.49, 29.11, 23.97, 23.58, 23.53, 23.11, 4.14 (Pd-Me). Anal. Calcd for C$_{39}$H$_{47}$ClN$_2$O$_2$Pd: C, 65.27; H, 6.60; N, 3.90; Found: C, 65.44; H, 6.35; N, 3.67.

General in Situ Activated Polymerization Procedure. A 350 mL glass thick-walled pressure vessel was charged with the required amount of MAO (for complexes **Ni-1−Ni-6**) or NaBAF (for complexes **Pd-1−Pd-6**), 50 mL of toluene, and a magnetic stir bar in the glovebox. The pressure vessel was connected to a high-pressure polymerization line, and the solution was degassed. The vessel was warmed to the desired temperature using an oil bath and allowed to equilibrate for 10 min. The metal complex was injected to initiate polymerization and stirred continuously for the desired time. The polymerization was quenched via the addition of MeOH (5 mL), and the polymer was precipitated using excess acidic MeOH (5% HCl in MeOH) and dried in a vacuum oven to constant weight. BD = $1000 \times 2(I_{CH3})/(3I_{CH2+CH} + 3I_{CH3})$. ^{1}H NMR: CH$_3$ (alkyl methyl, alk-CH$_3$, m, 0.77−0.95 ppm); CH$_2$ and CH (alk-CH and alk-CH$_2$, m, ca. 1.0−1.45 ppm).

Copolymerization of Ethylene and MA. In a typical procedure, a 50 mL round-bottom Schlenk flask with a stirring bar was heated for 3 h to 150 °C under vacuum and then cooled to room temperature. The flask was pressurized to 15 psi of ethylene and vented three times. The appropriate amounts of CH$_2$Cl$_2$ solvent, MA, and NaBAF were introduced into the glass reactor under an ethylene atmosphere, and then a 2 mL solution of the palladium catalyst (30 μmol) in CH$_2$Cl$_2$ was syringed into the well-stirred solution with the total reaction volume kept at 25 mL. The ethylene pressure was kept at a constant value of 15 psi by continuous feeding of gaseous ethylene throughout the reaction. The polymerizations were terminated by the addition of a large amount of methanol after continuous stirring for 15 h. Then the methanol was decanted off, and the sticky polymer was redissolved in hot toluene. The polymer solution was filtered through alumina and silica to remove catalyst residues. The resulting precipitated polymers were collected and treated by concentration and drying under vacuum at 40 °C to a constant weight. The MA incorporation (mol %) was calculated from ^{1}H NMR analysis, as was done before in previous studies of MA copolymers.[22] The branches ending with functional groups are added to the total branches. MA% = $4I_{OMe}/3(I_{CH3} + I_{CH2} + I_{CH}) \times 100\%$. ^{1}H NMR: OMe (s, ca. 3.61−3.76 ppm); CH$_2$ and CH (m, ca. 1.0−1.45 ppm); CH$_3$ (m, 0.77−0.95 ppm).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00202.

> Experimental procedures, NMR spectra for ligands, palladium complexes, polyethylene, and copolymers, and crystallographic data for complexes **Ni-1, Ni-5, Pd-1,** and **Pd-5** (PDF)
>
> Crystallographic data for complexes **Ni-1, Ni-5, Pd-1,** and **Pd-5** (ZIP)

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Notes

The authors declare no competing financial interest.

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