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Side-Arm Control in Phosphine-Sulfonate Palladium- and Nickel-Catalyzed Ethylene Polymerization and Copolymerization

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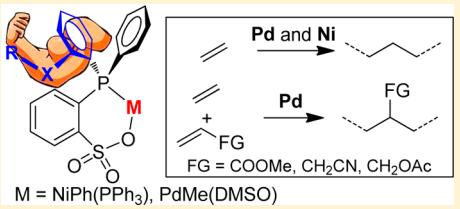
Supporting Information

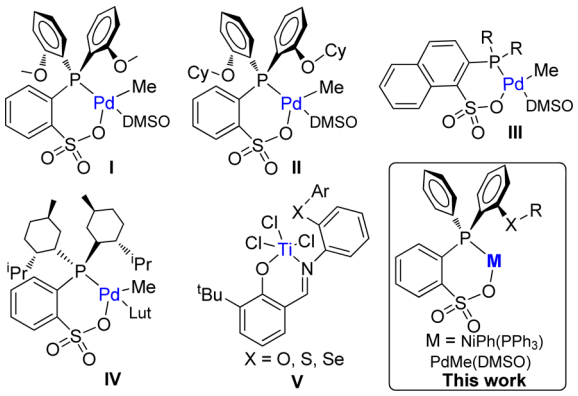
ABSTRACT: A series of phosphine-sulfonate ligands bearing various side-arm substituents were designed and prepared. The corresponding Pd(II) complexes [κ^2-(*P*,*O*)-2-(*P*PhAr)-1-benzenesulfonato]Pd(Me)(dmso) (**Pd1**, Ar = *o*-MeO-C_6H_4; **Pd2**, Ar = *o*-PhO-C_6H_4; **Pd3**, Ar = *o*-(2,6-Me_2-C_6H_3)O-C_6H_4; **Pd4**, Ar = *o*-$PhSO_2$-C_6H_4) and Ni(II) complexes [κ^2-(*P*,*O*)-2-(*P*PhAr)-1-benzenesulfonato]-NiPh(PPh_3) (**Ni1**, Ar = *o*-MeO-C_6H_4; **Ni2**, Ar = *o*-PhO-C_6H_4; **Ni3**, Ar = *o*-(2,6-Me_2-C_6H_3)O-C_6H_4; **Ni4**, Ar = *o*-$PhSO_2$-C_6H_4) were prepared and applied in ethylene polymerization and ethylene−polar monomer copolymerization. Catalysts **Pd2**, **Pd3**, **Ni2**, and **Ni3** are moderately active in ethylene polymerization (activity up to 8.7 × 10^5 g mol^{-1} h^{-1}), generating polyethylene with high molecular weights (M_n up to 105100) and high melting temperatures (T_m up to 131.6 °C). The two palladium catalysts can also initiate efficient copolymerization of ethylene with methyl acrylate, allyl cyanide, and allyl acetate. Most importantly, high copolymer molecular weights (M_n between 21600 and 82500) and high polar monomer incorporation ratios (between 6.1% and 15.2%) could be achieved simultaneously in this system. This side-arm strategy is highly effective in modulating the properties of the phosphine-sulfonate palladium and nickel catalysts.



INTRODUCTION

Transition-metal catalysts are of great importance in the field of olefin polymerization. The development of new catalysts is the key to the development of high-performance polyolefin materials. For example, α-diimine-based Pd and Ni catalysts enabled the synthesis of polyolefin materials with various topologies using ethylene as the only feedstock.[1] Most importantly, this class of catalysts can copolymerize ethylene with various polar monomers, leading to the generation of functionalized polyolefins.[1,2] Recently, palladium catalysts derived from phosphine-sulfonate and related ligands have emerged as powerful tools for the copolymerization of ethylene with a surprisingly broad range of polar monomers.[3] Despite the extensive studies on this class of catalysts, many examples suffer from low activity, low copolymer molecular weight, and/or low comonomer incorporation in the copolymerization reactions. For example, the benchmark dianisyl-substituted phosphine-sulfonate palladium catalyst (Chart 1, **I**) affords ethylene−methyl acrylate (E-MA) copolymer with a molecular weight (M_n) of ca. 4000.[4] The utilization of cyclohexyl (Chart 1, **II**), sterically bulky, or biaryl substituents on the phosphorus atom could increase the E-MA copolymer M_n value to ca. 47000.[5] Our group showed that a naphthalene backbone (Chart 1, **III**) could increase the copolymer molecular weight.[6] By utilizing a very bulky menthyl-phosphine-sulfonate ligand (Chart 1, **IV**), Nozaki et al. showed that very high E-MA copolymer M_n values (up to 177000) could be achieved at the expense of MA incorporation (0.6%).[7] Recently, Mecking et al. developed a strategy to enhance the copolymer molecular weight by taking advantage of the fast consecutive insertion of acrylic anhydride.[8]

Chart 1. Metal Catalysts Based on Different Phosphine-Sulfonate Ligands and Titanium Catalysts Containing Side-Arm Substituents



Tang et al. performed systematic works concerning the side-arm effect on a number of asymmetric transformations.[9] In addition to the core ligand coordination sphere, the introduction of an extra side-arm group in the metal complexes could alter the steric environment and the electronic properties of the metal center. It should be noted that the side arm could

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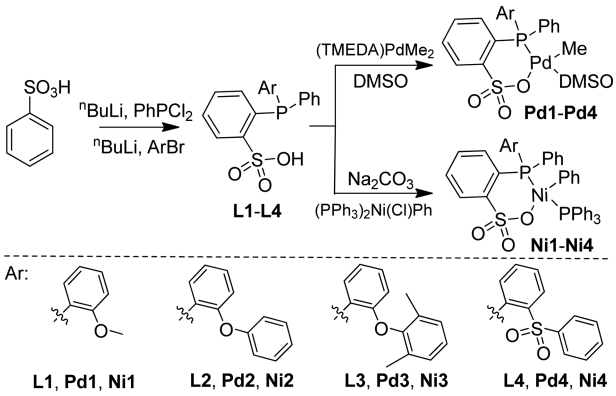
exert either a strong or a hemilabile coordination to the metal center. This side-arm strategy has also been applied in olefin polymerization and lactide polymerization reactions using Ti (Chart 1, **V**), Cr, Ni, Pd, Al, and other catalysts.[10]

Side arms containing two MeO substituents exist in the benchmark phosphine-sulfonate palladium catalyst (Chart 1, **I**). The Pd−O bond distance (3.52 Å)[11] is relatively close to the sum of the van der Waals radii of the Pd and O atoms (3.6 Å).[12] Because of the close proximity between the Pd and O, it is expected that the substituent on the O atom could exert some influence on the steric environment around the Pd center. In this contribution, a series of phosphine-sulfonate ligands bearing side arms with different electronic and steric perturbations were designed and synthesized. The properties of the corresponding palladium and nickel complexes in olefin polymerization and copolymerization reactions were investigated.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Pd and Ni Complexes. The phosphine-sulfonate ligands **L1**−**L4** could be easily synthesized from the sequential reactions of $PhPCl_2$ with lithiated benzenesulfonic acid and lithiated aryl compounds (Scheme 1). These ligands were characterized by ^1H, ^{13}C, and ^{31}P NMR, mass spectrometry, and elemental analysis. Subsequently, the reactions with the palladium and nickel precursors (TMEDA)$PdMe_2$ (TMEDA = tetramethylethylenediamine) and *trans*-[$(PPh_3)_2Ni(Cl)Ph$] led to the formation of the desired metal complexes **Pd1**−**Pd4** and **Ni1**−**Ni4** in moderate yields. These metal complexes were characterized by ^1H, ^{13}C, and ^{31}P NMR and elemental analysis.

Scheme 1. Synthesis of the Ligands and Metal Complexes



The molecular structures of **Pd3** and **Ni3** were determined by X-ray diffraction (Figure 1). Both metal centers adopt a square-planar geometry. The Pd1−O4 (3.49 Å) bond distance is slightly shorter than the sum of the van der Waals radii of the Pd and O atoms (3.6 Å).[12] In contrast, the Ni1−O4 (3.08 Å) bond distance is much shorter than the sum of the van der Waals radii of the Ni and O atoms (3.55 Å).[12] The metal−oxygen distances might be able to become shorter in solution and during polymerization. In both cases, the side-arm substituents clearly exert steric influence on the metal centers. In addition, this effect is hypothesized to be enhanced during the polymerization process after the dissociation of the coordinating bases (DMSO for Pd catalysts and PPh_3 for Ni catalysts).

Pd- and Ni-Catalyzed Ethylene Polymerization. The results from ethylene polymerization are summarized in Table 1. Catalyst **Pd1** showed relatively low activity, generating polyethylene with moderate molecular weight and moderate melting temperature (Table 1, entry 1). Interestingly, the catalytic activity was increased by more than 10 times by changing the methyl substituent in **Pd1** to a phenyl substituent in **Pd2** (Table 1, entry 2). In addition, the polyethylene molecular weight (M_n) was increased from 20000 to 42200, along with increased polymer melting temperature. With the 2,6-dimethylphenyl substituent, catalyst **Pd3** showed slightly reduced activity in comparison to **Pd2** (Table 1, entry 3). However, the polymer molecular weight (M_n) was further increased to 105000. Here, the ligand steric effect is probably the major influencing factor. The phenylsulfonyl-substituted catalyst **Pd4** showed further reduced activity and greatly reduced polymer molecular weight (Table 1, entry 4).

The nickel catalyst **Ni1** is not active for ethylene polymerization at 80 °C (Table 1, entry 5). Surprisingly, catalyst **Ni2**

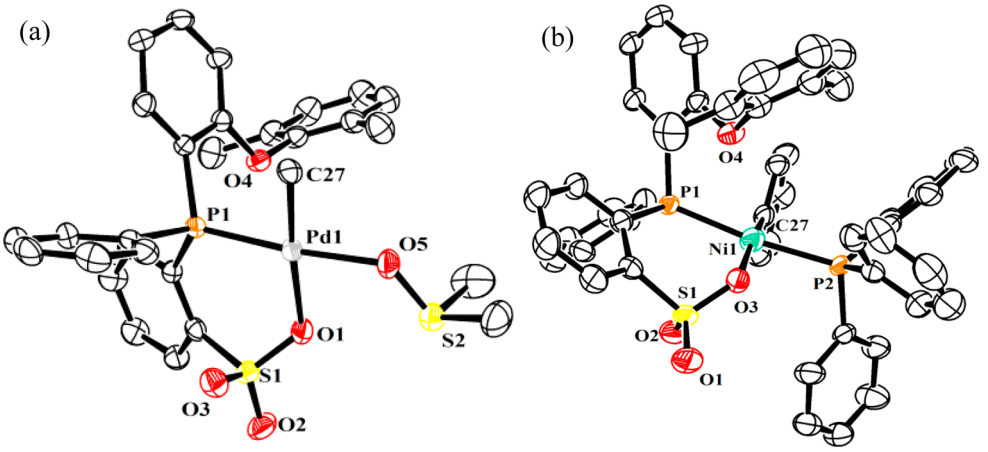


Figure 1. Molecular structures of **Pd3** (a) and **Ni3** (b). Selected bond lengths (Å) and angles (deg): **Pd3**, Pd(1)−C(27) = 2.042(4), Pd(1)−O(5) = 2.120(3), Pd(1)−O(1) = 2.148(3), Pd(1)−P(1) = 2.1906(11), C(27)−Pd(1)−O(5) = 85.87(14), O(1)−Pd(1)−P(1) = 96.50(8); **Ni3**, Ni1−C27 = 1.888(6), Ni1−O3 = 1.970(4), Ni1−P1 = 2.2223(18), Ni1−P2 = 2.2377(18), C27−Ni1−P2 = 87.79(18), O3−Ni1−P1 = 94.71(13). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

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Table 1. Ethylene Homopolymerization with Pd and Ni Complexes[a]

entry	T (°C)	cat.	yield (g)	act.[b]	M_n[c]	PDI[c]	T_m (°C)[d]
1	80	**Pd1**	0.8	0.8	20000	2.29	128.6
2	80	**Pd2**	8.7	8.7	42200	1.97	130.2
3	80	**Pd3**	5.2	5.20	105100	2.13	130.2
4	80	**Pd4**	3.7	3.71	7800	2.41	126.4
5	80	**Ni1**	0	0			
6	80	**Ni2**	1.8	1.8	1400	1.76	76.5
7	80	**Ni3**	3.6	3.6	5400	1.82	120.8
8	80	**Ni4**	0	0			
9	25	**Ni1**	0.07	0.07	1300	1.60	78.0
10[e]	25	**Ni2**	1.4	1.4	1500	1.43	83.6
11[e]	25	**Ni3**	1.2	1.2	9900	3.26	130.7
12[e]	25	**Ni4**	0	0			

[a]Polymerization conditions unless specified otherwise: catalyst, 10 μmol; toluene, 48 mL; CH_2Cl_2, 2 mL; ethylene, 8 atm; time, 1 h. [b]Activity in units of 10^5 g mol^{-1} h^{-1}. [c]Determined by GPC in trichlorobenzene at 150 °C. [d]Determined by differential scanning calorimetry (DSC). [e]Polymerization time 2 h.

with a phenyl substituent is highly active in ethylene polymerization without any cocatalysts (Table 1, entry 6). With the bulkier 2,6-dimethylphenyl substituent, both the activity and the polyethylene molecular weight were doubled for catalyst **Ni3** in comparison with catalyst **Ni2** (Table 1, entry 7). In addition, the polymer melting temperature was increased from 76.5 to 120.8 °C. At 25 °C, **Ni1** showed very low activity, generating polyethylene with low molecular weight and low melting temperature (Table 1, entry 9). In comparison with the results at 80 °C, catalysts **Ni2** and **Ni3** showed reduced activities (Table 1, entries 10 and 11). However, both the polyethylene molecular weights and the melting temperatures were dramatically increased. A difference of more than 50 °C in melting temperature was observed for the polyethylene generated by catalyst **Ni3** versus **Ni1**. Again, these differences are probably due to the steric effect of the side-arm substituents. Catalyst **Ni4** containing a phenylsulfonyl substituent is not active in ethylene polymerization at either 80 or 25 °C (Table 1, entries 8 and 12). If catalyst **Ni4** adopts a molecular structure similar to that of **Ni3**, the SO_2 moiety could orient in a position with very short Ni−O distance. The strong Ni−O interaction might be able to prevent ethylene coordination and shut down the polymerization.

Pd-Catalyzed Ethylene−Polar Monomer Copolymerization. The palladium catalysts **Pd1**−**Pd4** are also effective for the copolymerization of ethylene with methyl acrylate, allyl cyanide, and allyl acetate. Similarly to the homopolymerization results, catalysts **Pd2** and **Pd3** showed much better activities and polymer molecular weights in comparison to catalysts **Pd1** and **Pd4** (Table 2, entries 1−4). At higher MA concentration, the activities and copolymer molecular weights were decreased. However, the MA incorporation ratios were increased greatly (Table 2, entries 5−8). Interestingly and surprisingly, very high copolymer molecular weights (M_n between 21600 and 82500) and high comonomer incorporation ratios (between 6.1% and 15.2%) were achieved simultaneously for catalysts **Pd2** and **Pd3**. Moreover, the copolymer products are semicrystalline with high melting temperatures (up to 101.3 °C). When allyl cyanide or allyl acetate was used, low activities and low comonomer incorporation ratios were observed (Table 2, entries 9 and 10). However, the high copolymer molecular weights and high melting temperatures were maintained. The presence of these polar monomers completely shuts down nickel-catalyzed ethylene polymerization. This is probably due to the poisoning effect of the polar groups on the nickel center.

MA is incorporated in the copolymer main chain for catalysts **Pd1**−**Pd3** (Figure 2a). This is consistent with previously reported phosphine-sulfonate palladium catalysts.[3] For catalyst **Pd4**, ca. 30% of MA is incorporated into termination chain end groups (Figure 2b). This indicates that **Pd4** is more likely to undergo chain transfer after MA insertion in comparison with the other three palladium catalysts.

In transition-metal-catalyzed E-MA copolymerization, the copolymer molecular weight is always lower than that of the corresponding homopolymer.[1,3] Ethylene insertion at a tertiary carbon (from 2,1-MA insertion) is always slower than ethylene insertion into a secondary carbon (from ethylene insertion). Most important, chain transfer such as β-H elimination is more likely to happen when the insertion is slower (Scheme 2).

In the literature, one of the most widely used strategies to increase copolymer molecular weight is to increase the steric bulkiness of the ligands. This has proven to be effective in both the α-diimine and phosphine-sulfonate palladium systems.[1−3,13] However, the polar monomer incorporation ratio is usually dramatically reduced along with increased ligand sterics. In the area of metal-catalyzed ethylene−polar monomer copolymerization, it is highly challenging to solve the dilemma between

Table 2. Ethylene−Polar Monomer Copolymerization with the Pd Complexes[a]

entry	dat.	MA (M)	yield (mg)	act.[b]	X_{MA}[c] (%)	M_n[d]	PDI[d]	T_m (°C)[e]
1	**Pd1**	1	70	0.58	10.1	14600	2.10	86.4
2	**Pd2**	1	500	4.17	10.0	23700	2.04	90.9
3	**Pd3**	1	238	1.98	6.1	82500	1.54	101.3
4	**Pd4**	1	77	0.64	9.2	5600	1.50	80.9
5	**Pd1**	2	85	0.71	19.7	8400	1.41	
6	**Pd2**	2	180	1.50	15.2	21600	1.49	
7	**Pd3**	2	95	0.79	12.6	40200	1.68	77.3
8	**Pd4**	2	75	0.63	21.4	3400	1.13	
9[f]	**Pd3**	1	65	0.32	1.1	12800	1.79	128.0
10[g]	**Pd3**	1	63	0.31	3.3	12000	2.24	120.5

[a]Polymerization conditions: total volume of toluene and MA, 19 mL; CH_2Cl_2, 1 mL; catalyst, 12 μmol; ethylene, 8 atm; temperature, 80 °C; time, 1 h; 40 mg of BHT (butylated hydroxytoluene) for entries 1−4 and 80 mg of BHT for entries 5−8. [b]Activity in units of 10^4 g mol^{-1} h^{-1}. [c]Determined by ^1H NMR spectroscopy. [d]Determined by GPC in trichlorobenzene at 150 °C. [e]Determined by differential scanning calorimetry (DSC). [f]Allyl cyanide was used. [g]Allyl acetate was used.

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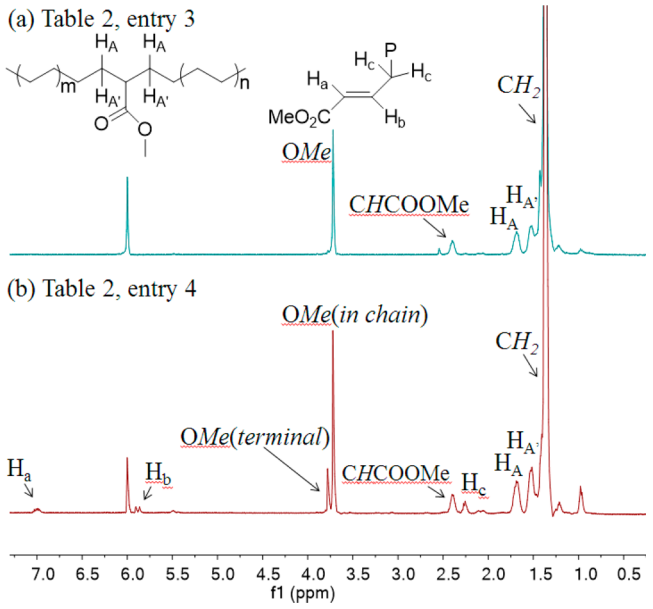
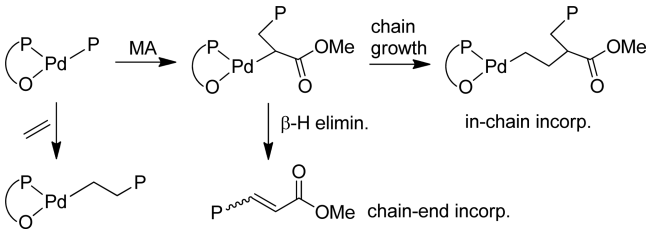


Figure 2. ^{1}H NMR spectra and the assignments of the E-MA copolymer samples generated by catalysts **Pd3** (a) and **Pd4** (b).

Scheme 2. Chain Growth and Chain Transfer Processes in Palladium-Catalyzed Ethylene Copolymerization with Methyl Acrylate



the copolymer molecular weight and the comonomer incorporation. In this system, it is expected that the sterically bulkier catalyst **Pd3** leads to higher copolymer molecular weights in comparison with catalysts **Pd2** and **Pd1**. Probably, steric effects play an important role in determining the properties of these metal catalysts. It is surprising that the comonomer incorporation ratio was only slightly reduced in the order **Pd1** > **Pd2** > **Pd3** (Table 2, entries 1−3 and 5−7). The unsymmetrical nature of the phosphine-sulfonate ligand framework (sterically very bulky phosphine side and sterically very open sulfonate side) and the flexible nature of the side arm substituent, as key ligand design features incorporated into these systems, are proposed to be responsible for this interesting effect. In addition, the interaction of the side arm oxygen atom with the metal center (as evidenced by the short metal−oxygen distance) might be able to retard β-H elimination and increase polymer molecular weight.[14]

CONCLUSIONS

To conclude, the side-arm strategy was successfully demonstrated in phosphine-sulfonate palladium- and nickel-catalyzed ethylene polymerization and copolymerization. By changes in the side-arm substituents, high-performance palladium and nickel catalysts were obtained. The catalysts containing phenyl and 2,6-dimethylphenyl substituents showed high activities and high polymer molecular weights in ethylene polymerization. In palladium-mediated ethylene−polar monomer copolymerization, both high copolymer molecular weights and high comonomer incorporation ratios could be realized. This study provides interesting insights for future studies addressing the dilemma between copolymer molecular weights and comonomer incorporation ratios.

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. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a Bruker Ascend 400 spectrometer at ambient temperature. The chemical shifts of the ^{1}H and ^{13}C NMR spectra were referenced to tetramethylsilane; the ^{31}P NMR spectra were referenced to an external 85% H_3PO_4 solution. Coupling constants are 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 were determined by gel permeation chromatography (GPC) with a PL-220 instrument equipped with two Agilent PLgel Olexis columns at 150 °C using *o*-dichlorobenzene as a solvent, and the calibration was made using a polystyrene standard. The values were corrected for linear polyethylene by universal calibration using the Mark−Houwink parameters of Rudin: $K = 1.75 \times 10^{-2}$ cm^3/g and $R = 0.67$ for polystyrene and $K = 5.90 \times 10^{-2}$ cm^3/g and $R = 0.69$ for polyethylene.[15] Dichloromethane, THF, and hexanes were purified by solvent purification systems. 2-Bromophenyl phenyl sulfide[16] and 1-bromo-2-(phenylsulfonyl)benzene were prepared according to literature procedures.[17]

Preparation of 2-Bromodiphenyl Ether. 2-Phenoxyaniline (1.85 g, 10 mmol) was dissolved in 48% aqueous HBr (7 mL). After the mixture was cooled to 0 °C, sodium nitrite (0.7 g, 10.26 mmol) was added slowly at 0 °C. This diazonium salt solution was poured into a flask containing CuBr (2 g, 13.95 mmol) and 5.8 mL of 48% aqueous HBr. The solution was heated to reflux for 5 h and extracted three times with CH_2Cl_2 (3 × 50 mL). The organic layers were washed with 1 mol L^{-1} NaOH (75 mL) and water (75 mL) and dried with $MgSO_4$. The solvent was removed to afford the crude product, which was purified by chromatography (petroleum ether/EtOAc 100/1) to afford the desired product (1.37 g, 55%). The NMR spectra of this compound agree well with the literature report.[18]

Preparation of 2-(2-Bromophenoxy)-1,3-dimethylbenzene. 2,6-Dimethylphenol (20 mmol, 2.44 g) was slowly added to a suspension of sodium hydride (60% in oil) (1 g, 25 mmol) in DMF (25 mL). The mixture was stirred for 30 min. 1-Bromo-2-fluorobenzene (20 mmol, 1.8 mL) was added, and the mixture was stirred at 160 °C for 24 h. Water (20 mL) was added to quench the reaction, and the organic layer was extracted with ethyl acetate. The organic and aqueous layers were separated, and the aqueous layer was extracted with ethyl acetate (150 mL). The combined organic solutions were washed with brine (50 mL) and water (50 mL) and dried with Na_2SO_4. The solvent was evaporated to afford the crude product, which was purified by chromatography (petroleum ether/EtOAc 100/1) to give the product (2.5 g, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, J = 7.9, 1.5 Hz, 1H), 7.23−6.99 (m, 4H), 6.86 (td, J = 7.8, 1.3 Hz, 1H), 6.37 (dd, J = 8.2, 1.3 Hz, 1H), 2.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.13 (s), 151.17 (s), 133.73 (s), 131.28 (s), 129.17 (s), 128.50 (s), 125.54 (s), 122.59 (s), 113.94 (s), 111.23 (s), 16.27 (s). HRMS (m/z): calcd for $C_{14}H_{14}BrO$, 277.0150; found, 277.0223 $[M + H]^+$. Anal. Calcd for $C_{14}H_{13}BrO$: C, 60.67; H, 4.73. Found: C, 60.41; H, 4.59.

Preparation of Ligand L1. At 0 °C, ^{n}BuLi (2.5 M, 8 mL, 20 mmol) was added slowly to a solution of benzenesulfonic acid (1.58 g, 10 mmol) in THF (25 mL). The suspension was stirred for 1 h before it was added to a solution of $PhPCl_2$ (1.35 mL, 10.0 mmol) in THF (30 mL) at −78 °C. The mixture was stirred for another 2 h at room

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temperature to yield a solution of lithium [chloro(phenyl)phosphino]-benzenesulfonate. 1-Bromo-2-methoxybenzene (1.86 g, 10 mmol) was dissolved in dry THF (20 mL) under nitrogen and cooled to −78 °C in a separate Schlenk. ^{n}BuLi (2.5 M in hexane, 4 mL, 10 mmol) was added dropwise. The resulting solution was stirred for 1.0 h at −78 °C before the lithium [chloro(phenyl)phosphino]benzenesulfonate solution was added dropwise. The mixture was stirred for another 24 h at room temperature. The volatiles were removed, and the residue was taken up in distilled water. The mixture was acidified with concentrated HCl/H_2O solution and extracted three times with CH_2Cl_2 (75 mL). The extracts were combined, dried over $MgSO_4$, and concentrated under vacuum. The crude product was recrystallized from dichloromethane/ether at room temperature. The resulting white powder was filtered and dried to give **L1** (2.2 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41−8.31 (m, 1H), 7.80−7.75 (m, 1H), 7.72 (dd, J = 16.2, 5.1 Hz, 2H), 7.54 (dd, J = 13.0, 5.9 Hz, 4H), 7.50−7.44 (m, 1H), 7.21 (dd, J = 14.7, 7.7 Hz, 1H), 7.17−7.05 (m, 3H), 3.77 (d, J = 11.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.24 (d, J = 1.9 Hz), 152.20 (d, J = 8.9 Hz), 137.25 (d, J = 1.4 Hz), 134.98 (d, J = 8.0 Hz), 134.80 (d, J = 2.8 Hz), 134.26 (d, J = 11.7 Hz), 134.07 (d, J = 2.9 Hz), 132.73 (d, J = 11.3 Hz), 129.84 (d, J = 13.0 Hz), δ 129.77 (d, J = 13.5 Hz). 128.82 (d, J = 9.2 Hz), 122.03 (d, J = 13.2 Hz), 118.27 (d, J = 91.0 Hz), 112.79 (d, J = 96.9 Hz), 112.04 (d, J = 6.1 Hz), 105.86 (d, J = 93.9 Hz), 56.43 (s). ^{31}P NMR (162 MHz, $CDCl_3$): δ −2.83 (s). ESI-MS (m/z): $[M - H]^-$ calcd for $C_{19}H_{16}O_4PS$, 371.0501; found, 371.0517. Anal. Calcd for $C_{19}H_{17}O_4PS$: C, 61.28; H, 4.60. Found: C, 61.08; H, 4.54.

Preparation of Ligand L2. A procedure similar to that for **L1** was employed except 2-bromodiphenyl ether (2.49 g, 10 mmol) was used. **L2** was obtained as a white solid (2.8 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (dd, J = 7.2, 5.1 Hz, 1H), 7.84−7.71 (m, 2H), 7.70−7.57 (m, 5H), 7.49 (m, 1H), 7.41−7.26 (m, 4H), 7.26−7.14 (m, 2H), 6.96−6.82 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.27 (d, J = 1.8 Hz), 153.93 (s), 152.79 (d, J = 9.0 Hz), 136.71 (d, J = 2.0 Hz), 135.25 (s), 135.17 (s), 134.75 (d, J = 12.1 Hz), 134.37 (d, J = 2.9 Hz), 133.15 (d, J = 11.3 Hz), 130.21 (s), 130.04 (d, J = 13.3 Hz), 129.84 (d, J = 13.2 Hz), 129.31 (d, J = 9.3 Hz), 125.72 (s), 123.92 (d, J = 13.4 Hz), 120.27 (s), 119.01 (d, J = 88.5 Hz), 116.67 (d, J = 6.2 Hz), 112.38 (d, J = 97.3 Hz), 108.48 (d, J = 97.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ −1.14. ESI-MS (m/z): $[M - H]^-$ calcd for $C_{24}H_{18}O_4PS$, 433.0658; found, 433.0660. Anal. Calcd for $C_{24}H_{19}O_4PS$: C, 66.35; H, 4.41. Found: C, 65.98; H, 4.37.

Preparation of Ligand L3. A procedure similar to that for **L1** was employed except 2-(2-bromophenoxy)-1,3-dimethylbenzene (2.77 g, 10 mmol) was used. **L3** was obtained as a white solid (2.3 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46−8.36 (m, 1H), 7.83−7.73 (m, 2H), 7.72−7.57 (m, 4H), 7.52 (dd, J = 15.0, 6.9 Hz, 2H), 7.39−7.26 (m, 2H), 7.23 (d, J = 7.0 Hz, 1H), 7.19−7.11 (m, 1H), 7.05 (d, J = 5.5 Hz, 1H), 6.99 (d, J = 5.3 Hz, 1H), 6.49 (t, J = 7.2 Hz, 1H), 2.01 (s, 3H, CH_3), 1.63 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.70 (s), 151.97 (d, J = 9.0 Hz), 148.78 (s), 136.57 (s), 134.75 (d, J = 12.5 Hz), 134.49 (d, J = 7.5 Hz), 134.20 (s), 132.93 (d, J = 11.2 Hz), 130.43 (d, J = 52.9 Hz), 129.89 (s), 129.80 (s), 129.68 (s), 129.10 (s), 128.76 (s), 128.69 (d, J = 9.7 Hz), 125.94 (s), 122.57 (d, J = 13.0 Hz), 118.36 (d, J = 86.9 Hz), 111.91 (d, J = 91.3 Hz), 105.89 (d, J = 95.7 Hz), 15.86 (s, CH_3), 15.42 (s, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ −2.25. ESI-MS (m/z): $[M - H]^-$ calcd for $C_{26}H_{22}O_4PS$, 461.0971; found: 461.0983. Anal. Calcd for $C_{26}H_{23}O_4PS$: C, 67.52; H, 5.01. Found: C, 67.23; H, 4.87.

Preparation of Ligand L4. A procedure similar to that for **L1** was employed except 1-bromo-2-(phenylsulfonyl)benzene (2.97 g, 10 mmol) was used. **L4** was obtained as a white solid (3.0 g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (dd, J = 7.7, 4.4 Hz, 1H), 8.18 (d, J = 7.5 Hz, 2H), 8.05−7.96 (m, 1H), 7.87−7.70 (m, 3H), 7.69−7.53 (m, 6H), 7.53−7.39 (m, 3H), 7.35−7.27 (m, 1H), 7.03 (m, 1H). ^{13}C NMR (100 MHz, DMSO): δ 151.80 (d, J = 26.5 Hz), 144.17 (d, J = 23.4 Hz), 141.50 (s), 140.47 (s), 140.17 (d, J = 8.5 Hz), 140.05 (s), 136.06 (s), 134.92 (s), 134.16 (d, J = 28.8 Hz), 133.45 (s), 133.26 (s), 133.03 (s), 130.23 (s), 129.21 (s), 128.98 (s), 128.51 (s), 128.45 (s), 128.29 (d, J = 6.3 Hz), 128.04 (s), 127.58 (d, J = 2.8 Hz). ^{31}P NMR (162 MHz, DMSO): δ −10.90. ESI-MS (m/z): $[M - H]^-$ calcd for $C_{24}H_{18}O_5PS_2$, 481.0328; found, 481.0330. Anal. Calcd for $C_{24}H_{19}O_5PS_2$: C, 59.74; H, 3.97; Found: C, 60.02; H, 4.23.

Preparation of Catalyst Pd1. $(TMEDA)PdMe_2$ (136 mg, 0.54 mmol) was added to a suspension of Ligand **L1** (200 mg, 0.54 mmol) in dioxane (5 mL) at room temperature. After 5 min, the evolution of gas stopped and the suspension turned clear. The solution was stirred for 1 h at room temperature. The resulting white precipitate was filtered, washed with diethyl ether, and dried under reduced pressure to yield the tmeda-bridged dimer **1-TMEDA** according to the literature.[4] **1-TMEDA** was dispersed in 5 mL of DMSO at room temperature. The solvent was removed under reduced pressure at 70 °C. After removal of DMSO under reduced pressure, the resulting solid was dispersed in diethyl ether, and isolated by filtration to yield a white solid (208 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (dd, J = 7.1, 4.6 Hz, 1H), 7.64 (dd, J = 12.3, 7.0 Hz, 2H), 7.56−7.40 (m, 5H), 7.34 (t, J = 7.6 Hz, 1H), 7.12 (dd, J = 10.8, 7.8 Hz, 1H), 6.95 (dd, J = 8.9, 4.7 Hz, 3H), 3.72 (s, 3H, *Me*O), 3.03 (s, 6H, DMSO-*H*), 0.46 (s, 3H, Pd-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.02 (d, J = 4.2 Hz), 148.16 (d, J = 14.1 Hz), 135.16 (d, J = 5.9 Hz), 134.83 (d, J = 12.9 Hz), 133.37 (d, J = 30.9 Hz), 131.01 (d, J = 22.8 Hz), 129.77 (d, J = 7.1 Hz), 128.71 (d, J = 11.6 Hz), 128.51 (d, J = 8.1 Hz), 128.42 (s), 128.25 (s), 127.80 (d, J = 9.4 Hz), 120.77 (d, J = 9.9 Hz), 117.87 (s), 117.29 (s), 111.59 (d, J = 4.6 Hz), 55.80 (s, MeO), 40.96 (s, DMSO), 1.74 (s, Pd-CH_3). ^{31}P NMR (162 MHz, DMSO): δ 21.32. Anal. Calcd for $C_{22}H_{25}O_5PPdS_2$: C, 46.28; H, 4.41. Found: C, 45.91; H, 4.23.

Preparation of Catalyst Pd2. A procedure similar to that for **Pd1** was employed except **L2** (200 mg, 0.47 mmol) was used. **Pd2** was obtained as a white solid (208 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23−8.13 (m, 1H), 7.72 (dd, J = 12.2, 7.4 Hz, 2H), 7.48 (dt, J = 14.9, 7.7 Hz, 5H), 7.34 (t, J = 7.4 Hz, 1H), 7.26−7.17 (m, 4H), 7.15−7.04 (m, 2H), 6.91 (dd, J = 7.8, 5.0 Hz, 1H), 6.82 (d, J = 7.9 Hz, 2H), 2.82 (s, 6H, DMSO-*H*), 0.56 (s, 3H, Pd-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.16 (d, J = 4.2 Hz), 155.20 (s), 148.15 (d, J = 14.4 Hz), 135.66 (d, J = 6.1 Hz), 134.99 (d, J = 12.9 Hz), 133.78 (s), 133.28 (s), 131.44 (s), 131.06 (s), 129.95 (s), 128.93 (d, J = 11.7 Hz), 128.49 (d, J = 8.1 Hz), 128.25 (s), 127.76 (s), 124.33 (s), 122.99 (d, J = 9.6 Hz), 120.69 (s), 120.13 (s), 119.40 (s), 117.57 (d, J = 4.5 Hz), 40.96 (s, DMSO), 2.72 (s, Pd-CH_3). ^{31}P NMR (162 MHz, DMSO): δ 21.49. Anal. Calcd for $C_{27}H_{27}O_5PPdS_2$: C, 51.23; H, 4.30. Found: C, 50.85; H, 4.80.

Preparation of Catalyst Pd3. A procedure similar to that for **Pd1** was employed except **L3** (200 mg, 0.43 mmol) was used. **Pd3** was obtained as a white solid (211 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (br, 1H), 7.82 (br, 2H), 7.49 (br, 4H), 7.32 (d, J = 42.2 Hz, 4H), 7.00 (d, J = 16.0 Hz, 4H), 6.39 (s, 1H), 2.94 (s, 6H, DMSO-*H*), 2.14 (s, 3H, Ph-*Me*), 1.61 (s, 3H, Ph-*Me*), 0.61 (s, 3H, Pd-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.86 (s), 150.14 (s), 148.20 (d, J = 16.5 Hz), 135.38 (d, J = 11.8 Hz), 134.07 (s), 133.39 (s), 131.31 (s), 130.96 (s), 130.02 (s), 129.28 (s), 129.07 (s), 128.75 (d, J = 11.6 Hz), 128.46 (s), 128.15 (s), 127.76 (s), 127.20 (s), 125.63 (s), 121.18 (d, J = 8.1 Hz), 116.99 (d, J = 55.2 Hz), 112.53 (s), 40.75 (s, DMSO), 17.34 (s, Ph-Me), 16.66 (s, Ph-Me), 2.74 (s, Pd-Me). ^{31}P NMR (162 MHz, DMSO): δ 20.66. Anal. Calcd for $C_{29}H_{31}O_5PPdS_2$: C, 52.69; H, 4.73. Found: C, 53.16; H, 4.54.

Preparation of Catalyst Pd4. A procedure similar to that for **Pd1** was employed except **L4** (200 mg, 0.41 mmol) was used. **Pd4** was obtained as a white solid (173 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (br, 1H), 7.98 (br, 1H), 7.73 (br, 2H), 7.67−7.38 (m, 10H), 7.30 (d, J = 7.7 Hz, 2H), 7.14−7.06 (m, 1H), 7.01 (d, J = 9.3 Hz, 1H), 2.89 (s, 6H, DMSO-*H*), 0.55 (s, 3H, Pd-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.38 (d, J = 15.3 Hz), 143.74 (d, J = 8.3 Hz), 140.98 (s), 135.80 (d, J = 5.2 Hz), 133.78 (s), 133.45 (d, J = 5.9 Hz), 133.10 (s), 132.27 (d, J = 7.3 Hz), 131.71 (s), 131.06 (s), 130.94 (s), 130.48 (s), 129.82 (d, J = 6.6 Hz), 129.47 (s), 129.29 (s), 129.16 (s), 128.98 (s), 128.90 (s), 128.66 (s), 128.09 (s), 41.30 (s, DMSO), 0.11 (s, Pd-CH_3). ^{31}P NMR (162 MHz, DMSO): δ 31.87. Anal. Calcd for $C_{27}H_{27}O_6PPdS_3$: C, 47.61; H, 4.00. Found: C, 47.36; H, 3.85.

Preparation of Catalyst Ni1. A suspension of **L1** (100 mg, 0.27 mmol) and Na_2CO_3 (86 mg, 0.81 mmol) in 10 mL of CH_2Cl_2 was

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stirred for 6 h at room temperature. *trans*-[$(PPh_3)_2Ni(Cl)Ph$] (187 mg, 0.27 mmol) was added in small portions. CH_2Cl_2 was added until the volume of the solution reached 15 mL, and the reaction mixture was stirred overnight at room temperature. The resulting yellow-orange mixture was filtered over Celite, and the volatiles were removed under vacuum. Toluene (3 mL) and hexanes (20 mL) were added to the orange residue, and the mixture was stirred for 2 h. The precipitate was recovered by filtration, washed with hexanes (3 × 10 mL), and dried for 20 h under dynamic vacuum to yield a yellow powder (150 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.67 (s, 1H), 7.46 (s, 8H), 7.34 (s, 6H), 7.26−7.15 (m, 6H), 7.00 (s, 4H), 6.81 (d, J = 27.5 Hz, 3H), 6.33 (s, 1H), 6.20 (d, J = 31.2 Hz, 2H), 6.02 (s, 1H), 3.85 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.16 (d, J = 285.3 Hz), −8.49 (d, J = 285.3 Hz). The solubility of **Ni1** is very poor in common organic solvents. Therefore, only ^{1}H and ^{31}P NMR data were collected. Anal. Calcd for $C_{43}H_{36}NiO_4P_2S$: C, 67.12; H, 4.72. Found: C, 67.36; H, 4.90.

Preparation of Catalyst Ni2. A procedure similar to that for **Ni1** was employed except **L2** (200 mg, 0.46 mmol) was used. **Ni2** was obtained as a yellow powder (268 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (br, 1H), 7.67 (br, 3H), 7.55 (br, 2H), 7.37 (d, J = 39.7 Hz, 12H), 7.15 (br, 8H), 7.07 (s, 1H), 6.97 (s, 2H), 6.84 (d, J = 18.4 Hz, 5H), 6.43 (br, 1H), 6.34 (br, 2H), 6.10 (br, 1H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.36 (d, J = 285.0 Hz), −8.56 (d, J = 285.0 Hz). The solubility of **Ni2** is poor in common organic solvents. Therefore, only ^{1}H and ^{31}P NMR data were collected. Anal. Calcd for $C_{48}H_{38}NiO_4P_2S$: C, 69.33; H, 4.61. Found: C, 69.06; H, 4.57.

Preparation of Catalyst Ni3. A procedure similar to that for **Ni1** was employed except **L3** (200 mg, 0.43 mmol) was used. **Ni3** was obtained as a yellow powder (277 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (br, 1H), 7.66 (br, 3H), 7.54 (s, 1H), 7.45 (br, 3H), 7.34 (br, 4H), 7.18 (br, 7H), 7.04 (br, 9H), 6.93 (br, 2H), 6.54 (d, J = 16.5 Hz, 2H), 6.34 (s, 2H), 6.13 (s, 2H), 2.21 (s, 3H, Ph-*Me*), 1.13 (s, 3H, Ph-*Me*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.76 (d, J = 7.7 Hz), 150.74 (s), 149.21 (d, J = 14.4 Hz), 138.81 (s), 138.48 (s), 135.08 (s), 134.48 (s), 134.37 (s), 134.20 (d, J = 9.0 Hz), 132.91 (s), 132.58 (s), 132.00 (s), 130.68 (s), 130.43 (s), 129.79 (d, J = 15.1 Hz), 129.79 (d, J = 15.1 Hz), 129.79 (d, J = 15.1 Hz), 129.40 (d, J = 11.6 Hz), 128.73 (d, J = 12.1 Hz), 128.02 (d, J = 9.6 Hz), 127.61 (d, J = 9.1 Hz), 126.78 (d, J = 5.9 Hz), 126.60 (s), 126.01 (d, J = 12.8 Hz), 122.03 (s), 121.29 (d, J = 6.2 Hz), 118.04 (d, J = 45.6 Hz), 113.00 (d, J = 3.3 Hz), 18.08 (s, Ph-Me), 15.14 (s, Ph-Me). ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.73 (d, J = 283 Hz), −10.58 (d, J = 283 Hz). Anal. Calcd for $C_{50}H_{42}NiO_4P_2S$: C, 69.86; H, 4.92. Found: C, 69.97; H, 5.09.

Preparation of Catalyst Ni4. A procedure similar to that for **Ni1** was employed except **L4** (200 mg, 0.41 mmol) was used. **Ni4** was obtained as a yellow powder (162 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (dd, J = 7.6, 3.8 Hz, 1H), 8.19 (br, 1H), 8.02 (dd, J = 7.1, 4.5 Hz, 1H), 7.82 (br, 2H), 7.67 (dd, J = 10.8, 7.2 Hz, 3H), 7.61−7.50 (m, 6H), 7.37 (dd, J = 13.0, 7.0 Hz, 5H), 7.29 (d, J = 6.9 Hz, 4H), 7.22−7.15 (m, 3H), 7.13−6.97 (m, 4H), 6.87 (d, J = 6.5 Hz, 1H), 6.78−6.66 (m, 2H), 6.58−6.47 (m, 2H), 6.29−6.13 (m, 2H), 5.96−5.86 (m, 1H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.03 (d, J = 279.5 Hz), 2.72 (d, J = 279.5 Hz). The solubility of **Ni4** is very poor in common organic solvents. Therefore, only ^{1}H and ^{31}P NMR data were collected. Anal. Calcd for $C_{48}H_{38}NiO_5P_2S_2$: C, 65.54; H, 4.35. Found: C, 65.79; H, 4.56.

Procedure for Ethylene Homopolymerization. In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with 48 mL of toluene and a magnetic stir bar in a glovebox. The vessel was connected to a high-pressure line, and the solution was degassed. The vessel was warmed to 80 °C using an oil bath (water bath for the case of polymerization at room temperature) and allowed to equilibrate for 15 min. A desired amount of the Pd or Ni complex in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe. With rapid stirring, the reactor was pressurized and maintained at 8.0 atm of ethylene. After the desired amount of time, the pressure vessel was vented and the polymer was precipitated using acidified methanol (methanol/HCl 50/1) and dried at 80 °C for 24 h under vacuum.

Procedure for ethylene-polar monomer copolymerization. In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with toluene, the desired amount of polar monomer, BHT (for the case of MA), and a magnetic stir bar in a glovebox. The pressure vessel was connected to a high-pressure line, and the solution was degassed. The vessel was warmed to the desired temperature using an oil bath and allowed to equilibrate for 5 min. A 12 μmol portion of the Pd complex in 2 mL of CH_2Cl_2 was injected into the polymerization system via syringe. With rapid stirring, the reactor was pressurized and maintained at the desired pressure of ethylene. After 1 h, the pressure vessel was vented and the polymer was precipitated in acidified methanol (methanol/HCl 50/1) and dried at 80 °C for 24 h under vacuum.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00294.

Experimental procedures, characterization data for ligands, metal complexes, polyethylene, and copolymers, and crystallographic data (PDF)

Accession Codes

CCDC 1509573 and 1526349 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414−6415. (b) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059−2062. (c) Camacho, D. H.; Guan, Z. *Chem. Commun.* **2010**, *46*, 7879−7893. (d) Ye, Z.; Xu, L.; Dong, Z.; Xiang, P. *Chem. Commun.* **2013**, *49*, 6235−6255. (e) Takeuchi, D. *Polym. J.* **2012**, *44*, 919−928. (f) Guo, L. H.; Chen, C. L. *Sci. China: Chem.* **2015**, *58*, 1663−1673. (g) Guo, L. H.; Dai, S. Y.; Sui, X. L.; Chen, C. L. *ACS Catal.* **2016**, *6*, 428−441.

(2) (a) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267−268. (b) Chen, C.; Luo, S.; Jordan, R. F. *J. Am. Chem. Soc.* **2008**, *130*, 12892−12893. (c) Chen, C.; Jordan, R. F. *J. Am. Chem. Soc.* **2010**, *132*, 10254−10255. (d) Chen, C.; Luo, S.; Jordan, R. F. *J. Am. Chem. Soc.* **2010**, *132*, 5273−5284. (e) Vaidya, T.; Klimovica, K.; LaPointe, A. M.; Keresztes, I.; Lobkovsky, E. B.; Daugulis, O.; Coates, G. W. *J. Am. Chem. Soc.* **2014**, *136*, 7213−7216. (f) Wang, R. K.; Sui, X. L.; Pang, W. M.; Chen, C. L. *ChemCatChem* **2016**, *8*, 434−440. (g) Wang, R. K.; Zhao, M. H.; Chen, C. L. *Polym. Chem.* **2016**, *7*, 3933−3938. (h) Zou, W. P.; Chen, C. L. *Organometallics* **2016**, *35*,

DOI: 10.1021/acs.organomet.7b00294
Organometallics XXXX, XXX, XXX−XXX

1794−1801. (i) Sui, X. L.; Hong, C. W.; Pang, W. M.; Chen, C. L. *Mater. Chem. Front.* **2017**, *1*, 967−972. (j) Na, Y. N.; Wang, X.; Lian, K.; Zhu, Y.; Li, W.; Luo, Y.; Chen, C. L. *ChemCatChem* **2017**, *9*, 1062−1066. (k) Takano, S.; Takeuchi, D.; Osakada, K.; Akamatsu, N.; Shishido, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 9246−9250. (l) Allen, K. E.; Campos, J.; Daugulis, O.; Brookhart, M. *ACS Catal.* **2015**, *5*, 456−464. (m) Long, B. K.; Eagan, J. M.; Mulzer, M.; Coates, G. W. *Angew. Chem.* **2016**, *128*, 7222−7226. (n) Chen, Z.; Liu, W. J.; Daugulis, O.; Brookhart, M. *J. Am. Chem. Soc.* **2016**, *138*, 16120−16129.

(3) (a) Nakamura, A.; Anselment, T. M. J.; Claverie, J.; Goodall, B.; Jordan, R. F.; Mecking, S.; Rieger, B.; Sen, A.; Van Leeuwen, P. W. N. M.; Nozaki, K. *Acc. Chem. Res.* **2013**, *46*, 1438−1449. (b) Zhang, Y. L.; Cao, Y. C.; Leng, X. B.; Chen, C.; Huang, Z. *Organometallics* **2014**, *33*, 3738−3745. (c) Sui, X. L.; Dai, S. Y.; Chen, C. L. *ACS Catal.* **2015**, *5*, 5932−5937. (d) Chen, M.; Yang, B. P.; Chen, C. L. *Angew. Chem., Int. Ed.* **2015**, *54*, 15520−15524. (e) Chen, M.; Yang, B. P.; Chen, C. L. *Synlett* **2016**, *27*, 1297−1302. (f) Nakano, R.; Nozaki, K. *J. Am. Chem. Soc.* **2015**, *137*, 10934−10937. (g) Ota, Y.; Ito, S.; Kobayashi, M.; Kitade, S.; Sakata, K.; Tayano, T.; Nozaki, K. *Angew. Chem., Int. Ed.* **2016**, *55*, 7505−7509. (h) Jian, Z.; Falivene, L.; Boffa, G.; Ortega Sánchez, S.; Caporaso, L.; Grassi, A.; Mecking, S. *Angew. Chem., Int. Ed.* **2016**, *55*, 14378−14383. (i) Wada, S.; Jordan, R. F. *Angew. Chem., Int. Ed.* **2017**, *56*, 1820−1824.

(4) Guironnet, D.; Roesle, P.; Runzi, T.; Gottker-Schnetmann, I.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 422−423.

(5) (a) Neuwald, B.; Falivene, L.; Caporaso, L.; Cavallo, L.; Mecking, S. *Chem. - Eur. J.* **2013**, *19*, 17773−17788. (b) Piche, L.; Daigle, J.-C.; Poli, R.; Claverie, J. P. *Eur. J. Inorg. Chem.* **2010**, *2010*, 4595−4601. (c) Skupov, K. M.; Marella, P. R.; Simard, M.; Yap, G. P. A.; Allen, N.; Conner, D.; Goodall, B. L.; Claverie, J. P. *Macromol. Rapid Commun.* **2007**, *28*, 2033−2038. (d) Piche, L.; Daigle, J.-C.; Rehse, G.; Claverie, J. P. *Chem. - Eur. J.* **2012**, *18*, 3277−3285.

(6) (a) Wu, Z. X.; Chen, M.; Chen, C. L. *Organometallics* **2016**, *35*, 1472−1479. (b) Wu, Z. X.; Hong, C. W.; Du, H.; Pang, W. M.; Chen, C. L. *Polymers* **2017**, *9*, 168.

(7) Ota, Y.; Ito, S.; Kuroda, J.; Okumura, Y.; Nozaki, K. *J. Am. Chem. Soc.* **2014**, *136*, 11898−11901.

(8) Jian, Z.; Baier, M. C.; Mecking, S. *J. Am. Chem. Soc.* **2015**, *137*, 2836−2839.

(9) Liao, S. H.; Sun, X. L.; Tang, Y. *Acc. Chem. Res.* **2014**, *47*, 2260−2272.

(10) (a) Wang, C.; Ma, Z.; Sun, X.-L.; Gao, Y.; Guo, Y.-H.; Tang, Y.; Shi, L.-P. *Organometallics* **2006**, *25*, 3259−3266. (b) Jones, D. J.; Gibson, V. C.; Green, S. M.; Maddox, P. J. *Chem. Commun.* **2002**, 1038−1039. (c) Li, W.; Sun, H.; Chen, M.; Wang, Z.; Hu, D.; Shen, Q.; Zhang, Y. *Organometallics* **2005**, *24*, 5925−5928. (d) Long, J. M.; Gao, H. Y.; Wu, Q. *Eur. J. Inorg. Chem.* **2008**, *2008*, 4296−4305. (e) Long, J. M.; Gao, H. Y.; Liu, F. S.; Song, K. M.; Hu, H.; Zhu, F. M.; Wu, Q. *Inorg. Chim. Acta* **2009**, *362*, 3035−3042. (f) Gallaway, J. B. L.; McRae, J. R. K.; Decken, A.; Shaver, M. P. *Can. J. Chem.* **2012**, *90*, 419−426. (g) Li, M.; Chen, M.; Chen, C. L. *Polymer* **2015**, *64*, 234−239. (h) Zhang, D.; Pang, W. M.; Chen, C. L. *J. Organomet. Chem.* **2017**, *836*−*837*, 56−61.

(11) Vela, J.; Lief, G. R.; Shen, Z.; Jordan, R. F. *Organometallics* **2007**, *26*, 6624−6635.

(12) Batsanov, S. S. *Inorg. Mater.* **2001**, *37*, 871−885.

(13) (a) Rhinehart, J. L.; Brown, L. A.; Long, B. K. *J. Am. Chem. Soc.* **2013**, *135*, 16316−16319. (b) Dai, S. Y.; Sui, X. L.; Chen, C. L. *Angew. Chem., Int. Ed.* **2015**, *54*, 9948−9953. (c) Dai, S. Y.; Zhou, S. X.; Zhang, W.; Chen, C. L. *Macromolecules* **2016**, *49*, 8855−8862. (d) Dai, S. Y.; Chen, C. L. *Angew. Chem., Int. Ed.* **2016**, *55*, 13281−13285. (e) Na, Y. N.; Zhang, D.; Chen, C. L. *Polym. Chem.* **2017**, *8*, 2405−2409. (f) Chen, M.; Chen, C. L. *ACS Catal.* **2017**, *7*, 1308−1312.

(14) (a) Stephenson, C. J.; McInnis, J. P.; Chen, C.; Weberski, M. P., Jr.; Motta, A.; Delferro, M.; Marks, T. J. *ACS Catal.* **2014**, *4*, 999−1003. (b) Popeney, C. S.; Rheingold, A. L.; Guan, Z. *Organometallics* **2009**, *28*, 4452−4463. (c) Bryliakov, K.; Talsi, E. P.; Möller, H. M.; Baier, M. C.; Mecking, S. *Organometallics* **2010**, *29*, 4428−4430.

(15) Grinshpun, V.; Rudin, A. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 219−223.

(16) Rout, L.; Sen, T. K.; Punniyamurthy, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 5583−5586.

(17) Szadkowska, A.; Zukowska, K.; Pazio, A. E.; Woźniak, K.; Kadyrov, R.; Grela, K. *Organometallics* **2011**, *30*, 1130−1138.

(18) Lockner, J. W.; Dixon, D. D.; Risgaard, R.; Baran, P. S. *Org. Lett.* **2011**, *13*, 5628−5631.

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