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Tan Chen, Pang Wen-Min, Chen Chang-Le

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A Phenol-containing α -Diimine Ligand for Nickel- and Palladium-Catalyzed Ethylene Polymerization

Chen Tan, Wen-Min Pang, and Chang-Le Chen*

Hefei National Laboratory for Physical Sciences at the Microscale, CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China

 Electronic Supplementary Information

Abstract A phenol-containing dibenzhydryl-based α -diimine ligand bearing hydroxy group on *para*-position of aniline moiety was designed, synthesized, and investigated in Ni- and Pd-catalyzed ethylene polymerization. The Ni complex bearing hydroxy groups resulted in not only high polyethylene molecular weight (M_n up to 1.5×10^6), but also significantly increased melting temperature (T_m up to 123 °C) and greatly decreased branching density (33/1000C) versus the Ni catalyst bearing OMe group on *para*-position of aniline moiety. This is consistent with the hypothesis that the deprotonation of the phenol moiety generated a phenoxide bearing strong electron-donating O^- substituent by methylaluminoxane (MAO) cocatalyst. The Pd complexes bearing hydroxy groups exhibited similar catalytic properties to those of the Pd catalyst bearing OMe groups did.

Keywords α -Diimine; Ethylene polymerization; Electronic effect; Palladium; Nickel

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INTRODUCTION

Substituent electronic effects play important roles in the design of molecular catalysts.^[1–17] In the field of transition metal catalyzed olefin polymerization, substituent electronic effects are widely investigated by introducing various electron-donating and withdrawing substituents (*e.g.* NMe₂, OMe, Me, H, Cl, CF₃, NO₂, *etc.*) to ligands, since electronic nature of the metal catalysts can efficiently modulate (co) polymerization processes as well as microstructures of polyolefin products.^[18–32] Furthermore, the polyolefin microstructures strongly influence the rheology and mechanical properties.^[31,33–40] For instance, the α -diimine palladium catalyst bearing an electron-donating *para*-substituent (Chart 1, I and II) resulted in the increased stability of catalyst and more linear topology of polyethylene, indicating inhibited β -hydride elimination and subsequent chain transfer.^[28–31] Moreover, the dibenzhydryl-based α -diimine nickel catalysts bearing electron-donating *para*-substituents (Chart 1, III) resulted in not only high thermal stability and high polyethylene molecular weight, but also more linear polyethylene topology associated with moderately increased melting temperature (T_m) (X = OMe: T_m up to 62 °C versus

X = Cl: T_m up to 48 °C).^[32] It has been indicated that a stronger electric donor could produce polyethylene with significantly increased T_m associated with improved thermal and mechanical properties.^[31,33–40]

Disubstituted amino groups have been frequently used as strong electron-donating groups in investigations of electronic effects in metal-catalyzed olefin polymerizations.^[26,28–30] By contrast, O^- groups derived from alcohols and phenols were generally neglected and underdeveloped, probably due to the reactivity of OH groups. However, it was demonstrated that O^- group exhibits strong electron-donating ability (Hammett substituent constant: $\sigma_p = -0.81$ for O^- group compared to $\sigma_p = -0.72$ for NEt₂ group) (Chart 1).^[41] In practice, some organic nonlinear optical materials bearing O^- groups have exhibited better performance than that of similar molecules bearing disubstituted amino groups.^[42–44] Consequently, it is fascinating to investigate the electron-donating effects of O^- groups in the field of metal-catalyzed olefin polymerizations.

In this contribution, a phenol-containing α -diimine ligand (L) bearing two *para*-hydroxy groups was designed and explored for nickel- and palladium-catalyzed ethylene polymerization. The nickel (L-Ni) and palladium (L-Pd) complexes (Chart 1) were prepared and characterized. It is hypothesized that in nickel-catalyzed ethylene polymerization, the deprotonation of hydroxy groups will generate aluminium phenoxide moieties bearing O–Al bonds when using the cocatalyst methylaluminoxane (MAO) (Scheme 1). According

* Corresponding author: E-mail changle@ustc.edu.cn

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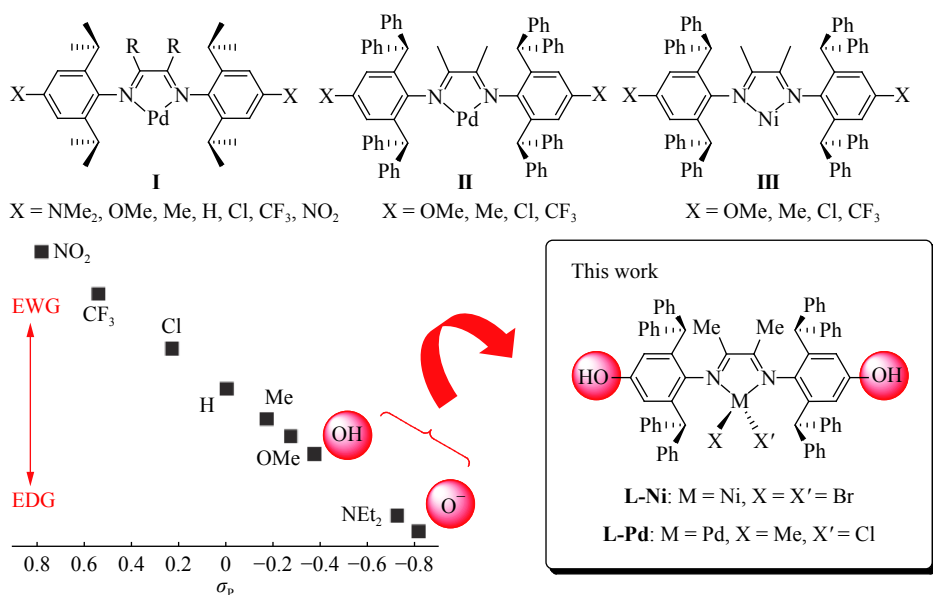
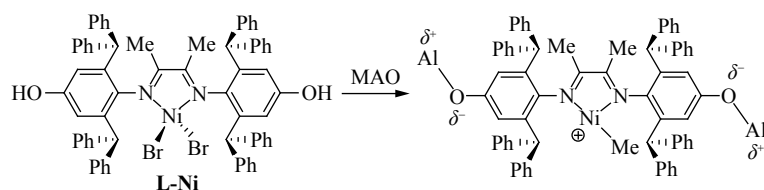


Chart 1 Selected α -diimine palladium and nickel catalysts for investigating electronic effects (EWG: electron-withdrawing group; EDG: electron-donating group)



Scheme 1 Activation of α -diimine Ni pre-catalyst with MAO and simultaneous deprotonation of OH groups

to the Pauling scale of electronegativity, the O—Al bonds are ionic bonds, since the electronegativity difference of oxygen and aluminium is greater than 1.7 ($\chi_{\text{Pauling,O}} - \chi_{\text{Pauling,Al}} = 1.93$),^[45–47] indicating the formation of strong electron-donating O^- groups. As a result, the polyethylene microstructures would be strongly influenced in **L-Ni** catalyzed ethylene polymerizations. By contrast, the palladium complex **L-Pd** is active in ethylene polymerization without the addition of MAO cocatalyst. Therefore, the catalytic properties of **L-Pd** should be similar to those of the corresponding Pd catalyst bearing OMe groups, since the Hammett substituent constants of OH ($\sigma_p = -0.37$) and OMe ($\sigma_p = -0.27$) are close to each other.^[41]

EXPERIMENTAL

Materials

All experiments were carried out under a dry nitrogen atmosphere by using standard Schlenk techniques or glovebox. Toluene was dried with sodium/benzophenone under nitrogen atmosphere and distilled before use. CH_2Cl_2 was pre-dried with Na_2SO_4 and distilled from CaH_2 under dry nitrogen. 2,6-Bis(diphenylmethyl)-4-anisidine,^[31] (COD) PdMeCl (COD = 1,5-cyclooctadiene),^[48] (DME)NiBr₂ (DME = 1,2-dimethoxyethane),^[49] and sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBAF)^[50] were prepared according to the reported procedures, respectively. Other

solvents and chemicals were purchased from J&K Chemical, Energy Chemical, and Nine Ding Chemistry Shanghai Co., Ltd., and were used as received.

Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 400 MHz spectrometer. ¹H-NMR and ¹³C-NMR chemical shifts were referenced to residual deuterated solvent resonance or tetramethylsilane signal (0 ppm). Elemental analyses were performed on a VarioELIII instrument. Mass spectra were obtained using electro spray ionization (ESI) LCMS-2010A. Matrix assisted laser desorption ionization time of flight mass spectroscopy (MALDI-TOF-MS) was performed on a Bruker ultrafleXtreme. X-ray diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.071$ nm). Molecular weight and molecular weight distribution of the polymer 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 140 °C using *o*-dichlorobenzene as solvent, and the calibration was made using polystyrene standard. Correction for linear polyethylene by universal calibration employed the Mark-Houwink parameters of Rudin: $K = 1.75 \times 10^{-2} \text{ cm}^3/\text{g}$ and $R = 0.67$ for polystyrene and $K = 5.90 \times 10^{-2} \text{ cm}^3/\text{g}$ and $R = 0.69$ for polyethylene.

Synthesis of 2,6-Bis(diphenylmethyl)-4-aminophenol (A)

At $-10\text{ }^{\circ}\text{C}$, BBr_3 (1.0 mol/L in CH_2Cl_2 , 25 mmol, 2.5 equiv.) was added slowly to a solution of 2,6-bis(diphenylmethyl)-4-anisidine (10 mmol) in CH_2Cl_2 (80 mL) under nitrogen. The mixture was stirred for 1 h at $-10\text{ }^{\circ}\text{C}$, moved to room temperature, and stirred for 4 h. Then the mixture was cooled to $-10\text{ }^{\circ}\text{C}$ and water (20 mL) was added slowly to the solution. After stirring for 12 h at room temperature, the mixture was extracted three times with CH_2Cl_2 . The extracts were combined, dried over $\text{MgSO}_4/\text{NaHCO}_3$, and concentrated under vacuum. The crude product was recrystallized from CH_2Cl_2 /hexanes at room temperature. The resulting white solid was filtered and dried to give 2,6-bis(diphenylmethyl)-4-aminophenol (A). Yield 98% (4.3 g). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, δ , ppm): 7.23–7.12 (m, 12H, aryl-H), 7.03 (d, $J = 8\text{ Hz}$, 4H, aryl-H), 6.96 (d, $J = 8\text{ Hz}$, 4H, aryl-H), 6.34 (s, 2H, aryl-H), 5.12 (s, 2H, CHPh_2). $^{13}\text{C-NMR}$ (d_6 -DMSO, 100 MHz, δ , ppm): 149.56, 143.20, 136.39, 129.69, 129.42, 128.86, 126.99, 116.47, 50.39. ESI-MS (m/z): 442.2154 $[\text{M}+\text{H}]^+$.

Synthesis of Ligand

A solution of 2,6-bis(diphenylmethyl)-4-aminophenol (A) (20 mmol), 2,3-butadione (10 mmol) and *p*-toluenesulfonic acid (50 mg) in toluene (100 mL) and ethanol (100 mL) was stirred at $80\text{ }^{\circ}\text{C}$ for 24 h, and then the reaction was refluxed with Dean-stark trap for 5 days, using MgSO_4 to remove water. The solvent was evaporated under reduced pressure. The crude product was recrystallized from CH_2Cl_2 /hexanes at room temperature. The resulting yellow solid was filtered and dried to give the desired ligand L. Yield 91% (8.5 g). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, δ , ppm): 7.25–7.14 (m, 26H, aryl-H), 7.04 (d, $J = 8\text{ Hz}$, 4H, aryl-H), 6.96 (d, $J = 8\text{ Hz}$, 4H, aryl-H), 6.47 (s, 4H, aryl-H), 5.25 (s, 4H, CHPh_2), 1.13 (s, 6H, $\text{N}=\text{CMe}$). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, δ , ppm): 170.65 ($\text{N}=\text{CMe}$), 151.59, 143.30, 142.55, 141.90, 129.64, 129.38, 128.67, 128.43, 128.15, 126.50, 126.22, 115.57, 51.63 (CHPh_2), 16.67 ($\text{N}=\text{CMe}$). ESI-MS (m/z): 933.4384 $[\text{M}+\text{H}]^+$.

Synthesis of Nickel Complex L-Ni

The ligand L (0.5 mmol) and $(\text{DME})\text{NiBr}_2$ (0.5 mmol) were stirred in 10 mL of CH_2Cl_2 for 2 days at $25\text{ }^{\circ}\text{C}$. The solvent was removed, and the resulting powder was washed with hexane (10 mL for 2 times) and dried under vacuum to obtain the brown solid L-Ni. Yield 92% (529 mg). MALDI-TOF-MS (m/z): 988.1507 $[\text{M}-2\text{Br}-2\text{H}]^+$. Anal. Calcd. for $\text{C}_{68}\text{H}_{56}\text{Br}_2\text{N}_2\text{NiO}_2$: C, 70.92; H, 4.90; N, 2.43; Found: C, 70.89; H, 4.93; N, 2.41 (%).

Synthesis of Palladium Complex L-Pd

To a solution of the ligand L (1 mmol) in dry CH_2Cl_2 (20 mL) was added 265 mg (1 mmol) of $(\text{COD})\text{PdMeCl}$. After stirring the mixture for 3 days at $25\text{ }^{\circ}\text{C}$, the complex L-Pd was isolated using column chromatography (CH_2Cl_2 /MeOH = 5/1, *V/V*). The pure compound was obtained as a red solid. Yield 72% (619 mg). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, δ , ppm): 7.45 (d, $J = 8\text{ Hz}$, 4H, aryl-H), 7.33 (d, $J = 8\text{ Hz}$, 4H, aryl-H), 7.25–7.04 (m, 34H, aryl-H), 6.69 (s, 2H, aryl-H), 6.45 (s, 2H, aryl-H), 5.95 (s, 2H, CHPh_2), 5.70 (s, 2H,

CHPh_2), 0.68 (s, 3H, Pd-Me), 0.36 (s, 3H, $\text{N}=\text{CMe}$), 0.14 (s, 3H, $\text{N}=\text{CMe}$). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, δ , ppm): 178.23 ($\text{N}=\text{CMe}$), 173.62 ($\text{N}=\text{CMe}$), 154.06, 153.22, 143.60, 142.17, 142.04, 141.93, 136.80, 136.73, 136.42, 135.91, 130.09, 129.86, 129.82, 129.62, 128.73, 128.67, 128.57, 128.28, 126.99, 126.72, 126.60, 126.49, 116.44, 116.32, 51.74 (CHPh_2), 51.44 (CHPh_2), 20.30 ($\text{N}=\text{CMe}$), 19.30 ($\text{N}=\text{CMe}$), 5.93 (Pd-Me). MALDI-TOF-MS (m/z): 1036.0029 $[\text{M-Me-Cl-2H}]^+$, 1070.9928 $[\text{M-Me-2H}]^+$. Anal. Calcd. for $\text{C}_{69}\text{H}_{59}\text{ClN}_2\text{O}_2\text{Pd}$: C, 76.02; H, 5.46; N, 2.57; Found: C, 76.09; H, 5.43; N, 2.55 (%).

Synthesis of Palladium Complex L-Pd^{MeCN}

To a stirred solution of L-Pd (0.20 mmol) in CH_2Cl_2 (10 mL) was added a solution of AgSbF_6 (1.2 equiv.) in anhydrous acetonitrile (1 mL). The reaction mixture was stirred at $25\text{ }^{\circ}\text{C}$ for 1 h and then filtered through Celite®. The solvent was evaporated under reduced pressure. The crude product was recrystallized from CH_2Cl_2 and hexanes to give a red solid. $^1\text{H-NMR}$ (CDCl_3 , 400 MHz, δ , ppm): 7.36 (d, $J = 8\text{ Hz}$, 4H, aryl-H), 7.24 (d, $J = 8\text{ Hz}$, 4H, aryl-H), 7.16–6.95 (m, 34H, aryl-H), 6.60 (s, 2H, aryl-H), 6.41 (s, 2H, aryl-H), 5.89 (s, 2H, CHPh_2), 5.52 (s, 2H, CHPh_2), 2.03 (s, 3H, PdNMe), 0.58 (s, 3H, Pd-Me), 0.31 (s, 3H, $\text{N}=\text{CMe}$), 0.10 (s, 3H, $\text{N}=\text{CMe}$). Yield 77% (205 mg). MALDI-TOF-MS (m/z): 1038.2174 $[\text{M-Me-MeCN}]^+$. Anal. Calcd. for $\text{C}_{71}\text{H}_{62}\text{F}_6\text{N}_3\text{O}_2\text{PdSb}$: C, 64.05; H, 4.69; N, 3.16; Found: C, 64.09; H, 4.63; N, 3.15 (%).

Procedure for Ethylene Polymerization

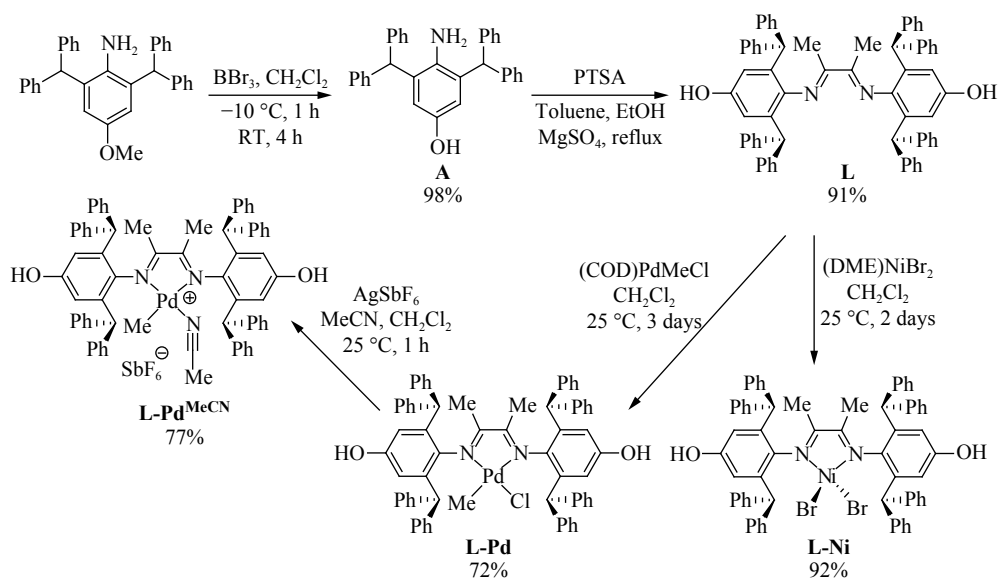
In a typical experiment, a 350 mL thick-walled glass pressure vessel was charged with cocatalyst (NaBAF or MAO), 20 mL of toluene, and a magnetic stir bar under an inert atmosphere. The vessel was pressurized with ethylene gas under stirring. Then pre-catalyst was injected to initiate polymerization and the mixture was stirred continuously for the desired time. The polymerization was quenched by adding ethanol (20 mL) and the polymer was precipitated and dried overnight in vacuum at $50\text{ }^{\circ}\text{C}$. Branching density (BD) was analyzed by using $^1\text{H-NMR}$ spectrum: $\text{BD} = 1000 \times (2/3) \times (I_{\text{CH}_3})/(I_{\text{CH}_2 \text{ and CH}} + I_{\text{CH}_3})$; δ (ppm): BDCH₃ (m, 0.77–0.95), CH₂ and CH (m, *ca.* 1.0–1.45).^[31]

RESULTS AND DISCUSSION

Synthesis and Characterization of Ligand and Pd, Ni Complexes

The aniline bearing a hydroxy group, 2,6-bis(diphenylmethyl)-4-aminophenol (A), was synthesized by the demethylation of 2,6-bis(diphenylmethyl)-4-anisidine using excess BBr_3 (yield 98%) (Scheme 2). The corresponding α -diimine ligand (L) was synthesized at a high temperature in toluene and ethanol using *p*-toluenesulfonic acid (PTSA) as catalyst (yield 91%). The ligand L was purified by recrystallization from CH_2Cl_2 /hexanes.

The Ni complex L-Ni was synthesized from the reaction of the ligand L with 1.0 equiv. of $(\text{DME})\text{NiBr}_2$ (DME = ethylene glycol dimethyl ether, Scheme 2), and characterized by MALDI-TOF-MS and elemental analysis. The Pd complex L-Pd was synthesized from the reaction of the ligand L with



Scheme 2 Synthesis of ligand and Pd, Ni complexes

1.0 equiv. of (COD)PdMeCl, and characterized by ^1H - and ^{13}C -NMR, MALDI-TOF-MS, and elemental analysis. The Pd complex **L-Pd**^{MeCN} was synthesized from the reaction of **L-Pd** with 1.2 equiv. of AgSbF₆ and excess MeCN, which was characterized by ^1H -NMR, MALDI-TOF-MS, elemental analysis, and X-ray crystallographic analysis (Fig. 1). The observed bond lengths [Å] are typical for α -diimine Pd(II) complexes: Pd1–N1 = 2.117(8), Pd1–N2 = 1.992(8), Pd1–N3 = 1.864(12), Pd1–C71 = 2.016(9), N3–C69 = 1.182(21). The palladium center exhibits a square-planar geometry with a N1–Pd1–N2 angle of 77.9(3)°, a N2–Pd1–C71 angle of 96.7(4)°, a N1–Pd1–N3 angle of 98.1(4)°, and a N3–Pd1–C71 angle of 87.4(4)°. The blockage of the axial positions at the metal center was observed.

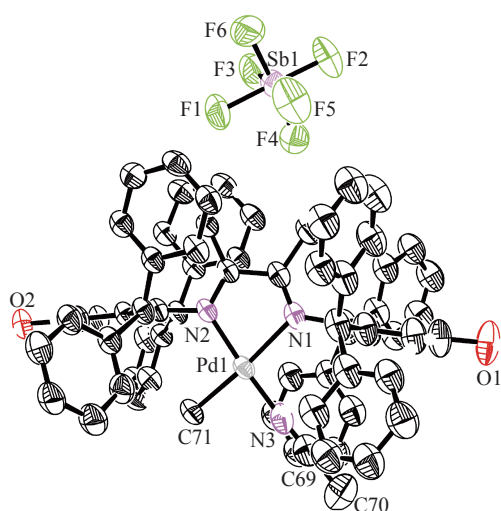


Fig. 1 Molecular structure of **L-Pd**^{MeCN} with 30% probability level (H atoms have been omitted for clarity^[61])

Ethylene Polymerization

The pre-catalyst **L-Ni** was directly *in situ* activated by using MAO in ethylene polymerization. Under the current condi-

tions, the catalyst derived from **L-Ni** exhibited high activities (Table 1, entries 1–4) comparable to the previously reported Ni catalysts bearing various *para*-substituents.^[32] More importantly, the high catalytic activity was maintained at temperatures up to 100 °C, making it suitable for industrially used gas-phase ethylene polymerizations (80–100 °C). Moreover, high molecular weight polyethylenes (M_n up to 1.5×10^6) were obtained by using **L-Ni**. Only trace amount of product was observed (Table 1, entries 5 and 6) by using AlEt₂Cl and AlEtCl₂ instead of MAO at 100 °C. **L-Ni** could catalyze ethylene polymerization using AlEt₂Cl at 40 °C. However, the catalytic activity decreased significantly with the increasing temperature and became trace activity at 100 °C, indicating poor thermostability of catalytic system using AlEt₂Cl (Fig. S1 in electronic supplementary information, ESI). Compared with the previously reported Ni catalyst bearing OMe group on *para*-position of aniline moiety,^[32] **L-Ni** produced polyethylene with significantly increased T_m (123 °C versus 62 °C at 40 °C; 120 °C versus 41 °C at 100 °C) (Fig. 2a) and greatly decreased branching density (33/1000C versus 48/1000C at 40 °C; 44/1000C versus 62/1000C at 100 °C). The Hammett constants can be used to quantitatively evaluate electronic effects of the substituents including O[−] group. Interestingly, the plot of polyethylene branching densities versus Hammett substituent constant (σ_p) for dibenzhydryl-based α -diimine Ni catalysts (Fig. 2b) indicates that the branching densities decreased approximately linearly with Hammett constants. According to previous works, in α -diimine Pd and Ni catalyzed ethylene polymerization, an electron-rich metal center would inhibit β -hydride elimination and subsequent chain transfer and result in more linear polymer topology.^[28–32,51–60] Control experiments showed that the reaction of MAO with *p*-tert-butylphenol in toluene produced a large amount of gaseous product (CH₄), indicating that MAO is able to generate phenoxide through deprotonation of the hydroxyl moiety. This could result in the increased electron density of the

Table 1 Ethylene polymerization catalyzed by phenol-containing α -diimine nickel and palladium catalysts

Entry ^a	Cat.	Temperature (°C)	Yield (g)	Activity ^b	$M_n^c \times 10^{-4}$	M_w/M_n^c	BD ^d	T_m^e (°C)
1	L-Ni	40	0.17	0.34	89.0	2.0	33	123
2	L-Ni	60	0.26	0.52	147.7	1.9	37	120
3	L-Ni	80	0.52	1.0	148.1	1.9	40	120
4	L-Ni	100	0.73	1.5	104.5	2.1	44	120
5 ^f	L-Ni	100	Trace	–	–	–	–	–
6 ^g	L-Ni	100	Trace	–	–	–	–	–
7	L-Pd	25	0.59	4.7	54.6	1.6	25	99
8	L-Pd	40	1.72	13.8	63.9	1.8	26	95
9	L-Pd	60	0.28	2.2	30.8	2.3	27	94
10	L-Pd	80	0.15	1.2	12.2	2.9	27	95

^a Polymerization conditions: For Ni: precatalyst = 1 μ mol; MAO = 600 μ mol (Al); reaction time = 30 min; ethylene pressure = 0.9 MPa; solvent: toluene = 50 mL and CH_2Cl_2 = 2 mL. For Pd: precatalyst = 5 μ mol; NaBAF = 6 μ mol; reaction time = 15 min; ethylene pressure = 0.9 MPa; solvent: toluene = 50 mL and CH_2Cl_2 = 2 mL; ^b Activity: $10^5 \text{ g}_{\text{polymer}}/(\text{mol}_{\text{Pd}} \cdot \text{h})$, $10^6 \text{ g}_{\text{polymer}}/(\text{mol}_{\text{Ni}} \cdot \text{h})$; ^c Determined by GPC in trichlorobenzene at 150 °C with polystyrene standards; ^d Branches per 1000C, which were determined by ¹H-NMR spectra; ^e Determined by differential scanning calorimetry (DSC; the second heating); ^f AlEt_2Cl was used instead of MAO; ^g AlEtCl_2 was used instead of MAO

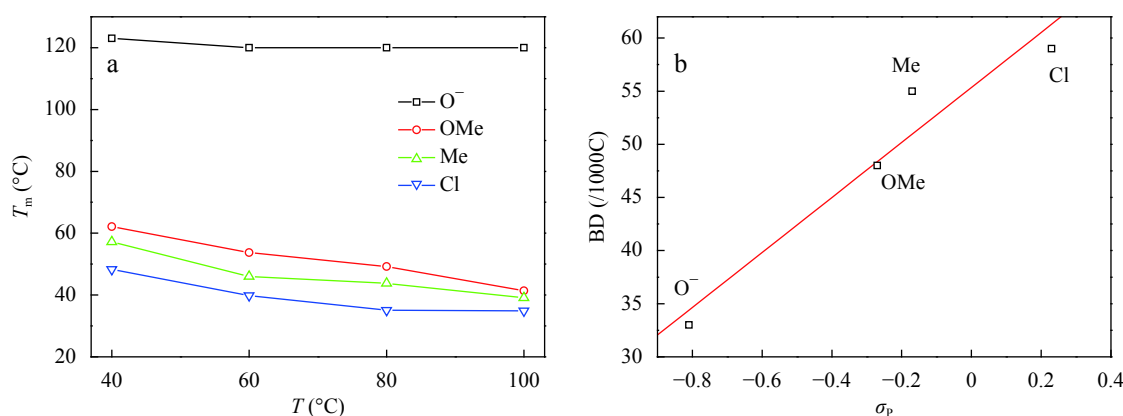


Fig. 2 (a) Plots of T_m s of polyethylene generated by using dibenzhydryl-based α -diimine Ni catalysts bearing various *para*-substituents versus polymerization temperature; (b) Plot of branching densities of polyethylene at 40 °C versus Hammett substituent constants for dibenzhydryl-based α -diimine Ni catalysts ($R = 0.97$)^[32]

nickel center, which subsequently affected the catalytic properties.

L-Pd is also highly active in ethylene polymerization as shown in Table 1, entries 7–10. However, T_m s and BDs of the polyethylene products were quite similar to those of the previously reported α -diimine Pd(II) catalyst bearing OMe group on *para*-position of aniline moiety.^[31] This could be explained by the similar Hammett substituent constants for OH ($\sigma_p = -0.37$) and OMe ($\sigma_p = -0.27$). These results supported our above-mentioned hypothesis that a strong electron-donating O^- substituent was generated in the nickel catalyst system through deprotonation of hydroxyl moiety by MAO cocatalyst. The catalyst **L-Pd** exhibited activities comparable to those of the reported Pd catalyst bearing OMe group (**PdOMe**) at 40 °C as well as room temperature (Table 1, entries 7 and 8).^[31] It resulted in lower activities than those of **PdOMe** at 60 and 80 °C (Table 1, entries 9 and 10),^[31] which might be due to the reactivity of acidic OH groups. The ethylene polymerization catalyzed by **PdOMe** with the addition of external *p-tert*-butylphenol indicated that the catalytic activity of **PdOMe** decreased with the increasing amount of external *p-tert*-butylphenol, and significantly decreased at higher polymerization temperature (Fig. S2, in ESI).

CONCLUSIONS

In summary, a phenol-containing α -diimine ligand (**L**) bearing two *para*-hydroxy groups and corresponding nickel (**L-Ni**) and palladium (**L-Pd**) catalysts were prepared, characterized, and explored in nickel- and palladium-catalyzed ethylene polymerizations. In Ni-catalyzed ethylene polymerization, the deprotonation of hydroxy groups generated aluminium phenoxide moieties bearing O–Al bonds by methylaluminumoxane (MAO). According to the Pauling scale of electronegativity, the O–Al bonds are ionic bonds, indicating the formation of strong electron-donating O^- groups. As a result, the nickel catalyst **L-Ni** resulted in significantly increased T_m (up to 123 °C) and greatly decreased polyethylene branching density (down to 33/1000C) compared to those of the Ni catalyst bearing OMe group on *para*-position of aniline moiety. By contrast, in **L-Pd** catalyzed ethylene polymerization, the melting temperatures and branching densities of polyethylene were similar to those of the OMe substituted α -diimine Pd(II) catalysts, since the Hammett substituent constants of OH and OMe were close to each other. We are currently working on the deprotonation of OH groups in the palladium system. It is envisaged that strong electron-donating O^- substituents will be applicable to other catalytic systems for olefin polymerizations.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2232-1>.

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