Supporting Information:

Ligand-Metal Secondary Interaction in Phosphine-Sulfonate Palladium and Nickel Catalyzed Ethylene (Co)Polymerization

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1. Experimental

**General**

All manipulations of air and moisture sensitive materials were performed under a dry N\textsubscript{2} atmosphere using a glove-box or standard Schlenk techniques. Ethylene gas was purified by passing through an Agilent oxygen/moisture trap. Solvents (tetrahydrofuran, toluene, hexanes) and deuterated solvents were dried before use. Other chemicals were purchased from J&K Chemical, Energy Chemical and Nine Ding Chemistry Shanghai Co. Ltd. and were used as received. \(N\)-(2-bromophenyl) carbazole\textsuperscript{1}, 1-(2-bromophenyl)-2,5-dimethylpyrrole\textsuperscript{2} Pd(TMEDA)Me\textsubscript{2}\textsuperscript{3} PdMeCl(COD)\textsuperscript{4} and trans-[(PPh\textsubscript{3})\textsubscript{2}Ni(Cl)Ph]\textsuperscript{5} were prepared using literature methods. Nuclear magnetic resonance (\(1^H, 13^C\) and \(31^P\) NMR) spectra were recorded on a Bruker 400 MHz spectrometer. \(1^H\) NMR and \(13^C\) NMR chemical shifts were referenced to residual deuterated solvent resonance or tetramethylsilane signal (0 ppm). \(31^P\) NMR chemical shifts were referenced to an external 85% H\textsubscript{3}PO\textsubscript{4} (aq.) standard. Elemental analyses were performed using a VarioELIII. Mass spectra were recorded on a Thermo LTQ Orbitrap XL (ESI\textsuperscript{+}). X-ray Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K\(\alpha\) radiation (\(\lambda = 0.71073\) Å). Molecular weight and molecular weight distribution of the polymer were determined by gel permeation chromatography (GPC) with a PL-220 equipped with two Agilent PLgel Olexis columns at 150 °C using o-dichlorobenzene as a solvent, and the calibration was made using polystyrene standard and are 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.\textsuperscript{6}

**Preparation of L1.** At 0 °C, \(\textsuperscript{t}BuLi\) (2.5 M in hexanes, 8 mL, 20 mmol) was added slowly to a solution of anhydrous benzenesulfonic acid (1.58 g, 10 mmol) in THF (25 mL). The suspension was stirred for 1 h before the addition of a solution of PhPCl\textsubscript{2} (0.87 mL, 20.0 mmol) in THF (30 mL) at -78 °C. The mixture was stirred for 1 h at -78 °C. \(N\)-(2-bromophenyl) carbazole (5.06 g, 20 mmol) was dissolved in dry THF (40 mL) under nitrogen and cooled to -78 °C. \(\textsuperscript{t}BuLi\) (2.5 M in hexanes, 8 mL, 20 mmol) was added dropwise. The resulting solution was stirred for 1 h at -78 °C before added
into the solution of lithium [chloro(phenyl)phosphino]benzenesulfonate. The mixture
was stirred for 1 h at -78 °C, and warmed room temperature and stirred for 24 h. The
volatiles were removed, and the residue was taken up in distilled water. The mixture
was acidified with concentrated HCl/H$_2$O solution, and extracted three times with
CH$_2$Cl$_2$. The extracts were combined, dried over MgSO$_4$, and concentrated under
vacuum. The crude product was recrystallized from CH$_2$Cl$_2$/ether at room temperature.
The resulting white powder was filtered and dried to give the desired ligand L1. Yield:
82%. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.38 (t, $J$ = 6 Hz, 1H), 8.00 (d, $J$ = 8 Hz, 1H), 7.90-
7.88 (m, 1H), 7.83 (d, $J$ = 4 Hz, 1H), 7.76-7.68 (m, 4H), 7.57-7.55 (m,1H), 7.34 (t, $J$ =
8 Hz, 2H), 7.23 (t, $J$ = 8 Hz, 1H), 7.13-7.05 (m, 4H), 6.94 (br, 2H), 6.63 (d, $J$ = 8Hz,
1H). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 3.70. $^{13}$C NMR (100 MHz, CDCl$_3$): 140.28 (d, $J$
= 5 Hz), 139.97 (s), 136.44 (s), 136.35 (s), 135.93 (d, $J$ = 2 Hz), 135.51 (d, $J$ = 3 Hz),
134.58 (s), 134.45 (s), 133.61 (d, $J$ = 2 Hz), 132.42 (s), 132.30 (s), 130.74 (s), 130.65
(s), 130.27 (s), 130.14 (s), 129.72 (s), 129.58 (s), 129.54 (s), 129.41 (s), 129.34 (s),
127.64 (s), 125.58 (s), 123.46 (s), 123.39 (s), 121.55 (s), 120.77 (s), 120.27 (s), 120.01
(s), 111.37 (d, $J$ = 1 Hz), 109.51 (s). ESI-MS (m/z): Anal. Calcd. for C$_{30}$H$_{22}$NO$_3$PS:
507.1058, found: 508.1131 ([M+H$^+$]).

Preparation of L2. At 0 °C, nBuLi (2.5 M, 20 mL, 50 mmol) was slowly added to a
solution of benzenesulfonic acid (3.95g, 25 mmol) in THF (100 mL). The suspension
was stirred for 1 h before the addition of a solution of PhPCl$_2$ (3.4 mL, 25 mmol) in
THF (20 mL) at -78 °C. The mixture was stirred for another 2 h at 25 °C to yield lithium
[chloro(phenyl)phosphino]benzenesulfonate. 1-(2-Bromophenyl)-2,5-dimethylpyrrole
(6.25g, 25mmol) was dissolved in dry THF (100 mL) under nitrogen. After cooling to
-78 °C, nBuLi (2.5 M in hexane, 4 mL, 10 mmol) was added dropwise. The resulting
solution was stirred for 1 h at -78 °C before adding to the lithium
[chloro(phenyl)phosphino]benzenesulfonate at -78 °C. The mixture was stirred for
another 24h at room temperature. THF was removed under vacuum, and the residue
was washed with CH$_2$Cl$_2$ and ether. The product was sensitive to air, and was used
directly for subsequent reactions. Yield: 69%. $^1$H NMR (400MHz, DMSO-d$_6$): $\delta$ 7.88
(br, 1H), 7.30-7.26 (m, 1H), 7.17 (t, $J$ = 8 Hz, 1H), 7.11-6.98 (m, 8H), 6.95-6.93 (m,
3H), 5.55 (s, 2H), 1.63 (s, 2H), 1.53 (s, 2H). $^{31}$P NMR (162 MHz, DMSO-d$_6$): -18.71.
$^{13}$C NMR (162 MHz, DMSO-d$_6$): 152.50 (d, $J$ = 26 Hz), 148.13 (s), 141.83 (d, $J$ = 25
Hz), 140.47 (d, $J$ = 20 Hz), 138.61 (d, $J$ = 17 Hz), 134.97 (s), 134.73 (s), 134.39 (s),
129.42 (s), 129.14 (s), 128.93 (s), 128.64 (s), 128.59 (s), 128.11 (s), 128.05 (s), 127.77 (s), 127.56 (s), 125.60 (s), 105.31 (d, $J = 10$ Hz), 13.60 (d, $J = 7$ Hz), 12.49 (d, $J = 2$ Hz). MALDI-TOF-MS (m/z): Anal. Calcd. for $C_{24}H_{21}NO_3PSLi$: 441.1140, found: 441.1260.

**Preparation of Pd1.** Ligand L1 (0.5 mmol) was suspended in 1,4-dioxane (4 mL). Pd(TMEDA)Me$_2$ (132 mg, 1.05 eq) was added at room temperature. Then the solution was stirred at -5 °C for 8 h and the solution became turbid. The resulting white precipitate was filtered, washed with diethyl ether and dried under reduced pressure. The solid was dissolved in DMSO (4 mL) at room temperature. The solvent was removed under reduced pressure at 80 °C. After the removing DMSO, the resulting solid was dispersed in diethyl ether, and isolated by filtration to yield an off-white solid. Yield: 75%. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.10 (br, 1H), 8.01 (d, $J = 8$ Hz, 1H), 7.95 (br, 1H), 7.70-7.52 (m, 3H), 7.44-7.33 (m, 7H), 7.25-7.13 (m, 4H), 6.88-6.86 (m, 1H), 6.69 (br, 1H), 2.67 (s, 6H), -0.22 (s, 3H). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 23.52. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.13 (d, $J = 5$ Hz), 142.70 (s), 142.24 (s), 134.59 (d, $J = 12$ Hz), 134.09 (d, $J = 7$ Hz), 133.26 (s), 132.10 (d, $J = 4$ Hz), 131.09 (s), 130.77 (s), 129.84 (s), 129.18 (s), 128.61 (s), 128.54 (s), 128.44 (s), 128.41 (s), 128.37 (s), 126.49 (s), 125.96 (s), 125.86 (s), 124.36 (d, $J = 2$ Hz), 124.02 (s), 120.30 (s), 120.23 (s), 120.15 (s), 120.09 (s), 120.01 (s), 112.65 (d, $J = 10$ Hz), 111.08 (s), 41.11 (s), 0.13 (s). Anal. Calcd. for $C_{33}H_{30}NO_4PPdS_2$: C, 56.13; H, 4.28; N, 1.98 Found: C, 56.02; H, 4.33; N, 2.03.

**Preparation of Ni1.** A suspension of ligand L1 (0.5 mmol) and Na$_2$CO$_3$ (159mg, 1.5 mmol) in 15 ml CH$_2$Cl$_2$ was stirred for 8 h at room temperature. Solid trans-[PPP$_3$_2Ni(Cl)Ph] (347mg, 0.5 mmol) was added in small portions. The reaction was stirred for 8 h at room temperature. The resulting orange mixture was filtered over Celite and the volatiles were removed under vacuum. Toluene (3 mL) was added to the orange residue to afford a slurry, then hexanes (20 mL) were added and the mixture was stirred for 2 h. The precipitate was recovered by filtration, washed with hexanes (3 x 10 ml) and dried under vacuum to yield an off-white solid. Yield: 62%. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.19 (dd, $J = 12$ Hz, $J = 8$ Hz, 1H), 7.84 (t, $J = 8$ Hz, 2H), 7.70-7.52 (m, 5H), 7.48-7.45 (m, 2H), 7.39-7.28 (m, 12H), 7.19-7.09 (m, 6H), 7.07-6.94 (m, 5H), 6.69-6.63 (m, 2H), 6.56 (t, $J = 8$ Hz, 2H), 6.44 (d, $J = 8$ Hz, 1H), 6.37 (t, $J = 8$ Hz,
1H), 6.24 (t, J = 8 Hz, 1H), 6.09 (t, J = 8 Hz, 1H). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 13.90 (d, J = 282 Hz), -0.46 (d, J = 282 Hz). $^{13}$C NMR (100 MHz, $d^6$-DMSO) $\delta$ 141.51 (s), 141.36 (d, J = 1Hz), 140.13 (s), 134.55 (s), 134.16 (s), 133.94 (s), 133.18 (s), 133.03 (s), 131.99 (s), 131.43 (d, J = 9 Hz), 129.43 (s), 129.26 (s), 128.87 (s), 128.83 (s), 128.76 (s), 128.64 (s), 128.61 (s), 128.58 (s), 128.50 (s), 128.34 (s), 128.29 (s), 128.23 (s), 128.14 (s), 128.02 (d, J = 2Hz), 127.95 (s), 127.65 (s), 127.54 (d, J = 1Hz), 127.36 (s), 126.62 (s), 125.57 (s), 125.25 (s), 124.87 (s), 122.92 (s), 122.46 (s), 119.56 (s), 119.35 (s), 119.21 (s), 119.02 (s), 113.60 (d, J = 5Hz), 110.20 (s). Anal. Calcd. for C$_{54}$H$_{41}$NO$_3$P$_2$NiS: C, 71.70; H, 4.57; N, 1.55. Found: C, 71.62; H, 4.68; N, 1.52.

Preparation of Pd$_2$. At room temperature, a 25 mL Schlenk tube was charged with 0.5 mmol PdMeCl(COD), 0.5 mmol L2 and 20 mL CH$_2$Cl$_2$. The solution was stirred for 10 min, and 156 mg (2.0 mmol, 2 equiv) of DMSO was added. The solution was further stirred for 10 min and was filtered through a syringe filter. The solution was evaporated, and the resulting solid was washed with ether. The solid was dissolved in CH$_2$Cl$_2$ (10 mL), and 3 equiv. of AgBF$_4$ was added. The solution was stirred for 10 min and was filtered through a syringe filter. The solvent was removed. The resulting solid was washed with ether and hexanes, and dried under vacuum to give Pd$_2$. Yield: 52%. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.14 (br, 1H), 7.56-7.53 (m, 1H), 7.45-7.36 (m, 7H), 7.17 (t, J = 8 Hz, 1H), 7.08 (t, J = 8 Hz, 1H), 6.52-6.47 (m, 1H), 6.08 (br, 1H), 5.66 (br, 1H), 2.68 (br, 6H), 2.38 (br, 3H), 1.36 (br, 3H), 0.51 (br, 3H). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 21.21. $^{13}$C NMR (100 MHz, $d^6$-DMSO): 148.96 (d, J = 14 Hz), 142.52(d, J = 9 Hz), 135.94 (d, J = 7 Hz), 134.62 (s), 134.50 (s), 134.01 (d, J = 2 Hz), 131.89 (d, J = 6 Hz), 131.81 (s), 130.86 (d, J = 1 Hz), 130.40 (s), 129.62 (s), 129.52 (s), 129.34 (s), 129.09 (s), 128.59 (s), 128.33 (s), 128.22 (s), 128.00 (d, J = 8 Hz), 127.23 (d, J = 8 Hz), 107.27 (s), 106.63 (s), 40.43 (s), 14.31 (s), 13.06 (s). Anal. Calcd. for C$_{27}$H$_{30}$NO$_4$PPdS$_2$: C, 51.15; H, 4.77; N, 2.21 Found: C, 51.09; H, 4.85; N, 2.17.

Procedure for ethylene homopolymerization. Polymerizations were performed in a Biotage Endeavor housed in a nitrogen-filled glovebox with eight parallel reactors and an overhead stirrer. In a typical experiment, the reaction vessels were charged with desired amount of catalyst in DCM (0.2 mL) and toluene (3
mL). The vessel was heated to 80 °C and allowed to equilibrate for 5 min. With rapid stirring, the vessel was pressurized and maintained at 8.0 atm of ethylene. After 1 h, the pressure vessel was vented and the polymer was precipitated in methanol and dried at 50 °C for 24 h under vacuum. Polymer-branching (B) density was determined by 1H NMR spectroscopy. B = 1000 × (2/3) ×(I\textsubscript{CH3})/(I\textsubscript{CH2-CH}+I\textsubscript{CH3}). CH\textsubscript{3} (m, 0.77–0.95 ppm); CH\textsubscript{2} and CH (m, ~1.0–1.45 ppm). For the low molecular weight polymers and oligomers, chain end groups were excluded. The branches were calculated according to the following equation.\textsuperscript{7,8}

\[
\frac{\text{Branches}}{1000^\circ} = \frac{2 \times 1000 \times I_{CH}}{3 + I_{CH_3+CH} + I_{CH_2} + I_{CH_3,\text{allyl}} + 2 \times (I_{CH_2,\text{vinyl}} + I_{CH_2,\text{vinylene}})}
\]

\[
I_{CH} = \frac{I_{CH_3}}{3} - \frac{I_{CH_2,\text{vinyl}}}{2} - I_{CH_2,\text{vinylene}}
\]

**Procedure for copolymerization of ethylene with polar comonomers.** In a typical experiment, the reaction vessels were charged with desired amount of catalyst and comonomer (for MA and AA, 20 mg of BHT, i.e. butylated hydroxytoluene, was added) in DCM (0.2 mL) and toluene (3 mL). The vessels were heated to 80 °C and allowed to equilibrate for 5 min. With rapid stirring, the vessel was pressurized and maintained at 8.0 atm of ethylene. After 1 h, the pressure vessel was vented and the polymer was precipitated in ethanol and dried at 50 °C for 24 h under vacuum. The incorporation ratio was calculated by 1H NMR analysis.
2. X-ray Crystallographic Studies

![Image of a molecular structure]

**Table S1** Crystal data and structure refinement for Pd1.

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3. NMR spectra of ligands and catalysts.

Figure S1 $^1$H NMR of L1.

Figure S2 $^{31}$P NMR of L1.
**Figure S3** $^{13}$C NMR of L1.

**Figure S4** ESI-MS of L1.
Figure S5 $^1$H NMR of L2-Li.

Figure S6 $^{31}$P NMR of L2-Li.
Figure S7 $^{13}$C NMR of L2-Li.

Figure S8 MALDI-TOF-MS of L2-Li.
Figure S9 $^1$H NMR of Pd1.

Figure S10 $^{31}$P NMR of Pd1.
Figure S11 $^{13}$C NMR of Pd1.

Figure S12 $^1$H NMR of Ni1.
Figure S13 $^{31}$P NMR of Ni1.

Figure S14 $^{13}$C NMR of Ni1.
Figure S15 $^1$H NMR of Pd2.

Figure S16 $^{31}$P NMR of Pd2.
Figure S17 $^{13}$C NMR of Pd2.
4. $^1$H NMR Spectra of Polymers

**Figure S18** $^1$H NMR of the polymer (table 1, entry 1).

**Figure S19** $^1$H NMR of the polymer (table 1, entry 2).
Figure S20 $^1$H NMR of the polymer (table 1, entry 3).

Figure S21 $^1$H NMR of the polymer (table 1, entry 4).
Figure S22. $^1$H NMR of the polymer (table 1, entry 7).

Figure S23. $^1$H NMR of the polymer (table 1, entry 8).
Figure S24 $^1$H NMR of the copolymer (table 2, entry 1).

Figure S25 $^1$H NMR of the copolymer (table 2, entry 2).
Figure S26 $^1$H NMR of the copolymer (table 2, entry 3).

Figure S27 $^1$H NMR of the copolymer (table 2, entry 4).
Figure S28 $^1$H NMR of the copolymer (table 2, entry 5).

Figure S29 $^1$H NMR of the copolymer (table 2, entry 6).
**Figure S30** $^1$H NMR of the copolymer (table 2, entry 7).

**Figure S31** $^1$H NMR of the copolymer (table 2, entry 8).
**Figure S32** $^1$H NMR of the copolymer (table 2, entry 9).

**Figure S33** $^1$H NMR of the copolymer (table 2, entry 10).
Figure S34 $^1$H NMR of the copolymer (table 2, entry 11).
5. GPC of Polymers

Figure S35 GPC of the polymer (table 1, entry 1).

Figure S36 GPC of the polymer (table 1, entry 2).
**Figure S37** GPC of the polymer (table 1, entry 3).

**Figure S38** GPC of the polymer (table 1, entry 5).
Figure S39 GPC of the polymer (table 1, entry 6).

Figure S40 GPC of the polymer (table 2, entry 1).
**Figure S41** GPC of the polymer (table 2, entry 2).

**Figure S42** GPC of the polymer (table 2, entry 3).
**Figure S43** GPC of the polymer (table 2, entry 4).

**Figure S44** GPC of the polymer (table 2, entry 5).
Figure S45 GPC of the polymer (table 2, entry 6).

Figure S46 GPC of the polymer (table 2, entry 7).
**Figure S47** GPC of the polymer (table 2, entry 8).

**Figure S48** GPC of the polymer (table 2, entry 9).
Figure S49 GPC of the polymer (table 2, entry 10).

Figure S50 GPC of the polymer (table 2, entry 11).
6. DSC of Polymers

Figure S51 DSC of the polymer (table 1, entry 1).

Figure S52 DSC of the polymer (table 1, entry 2).
Figure S53 DSC of the polymer (table 1, entry 3).

Figure S54 DSC of the polymer (table 1, entry 4).
Figure S55 DSC of the polymer (table 1, entry 5).

Figure S56 DSC of the polymer (table 1, entry 6).
Figure S57 DSC of the polymer (table 1, entry 7).

Figure S58 DSC of the polymer (table 1, entry 8).
**Figure S59** DSC of the polymer (table 2, entry 1).

**Figure S60** DSC of the polymer (table 2, entry 2).
Figure S61 DSC of the polymer (table 2, entry 3).

Figure S62 DSC of the polymer (table 2, entry 4).
Figure S63 DSC of the polymer (table 2, entry 5).

Figure S64 DSC of the polymer (table 2, entry 6).
Figure S65 DSC of the polymer (table 2, entry 7).

Figure S66 DSC of the polymer (table 2, entry 8).
Figure S67 DSC of the polymer (table 2, entry 9).

Figure S68 DSC of the polymer (table 2, entry 10).
Figure S69 DSC of the polymer (table 2, entry 11).
7. References