Supplementary Information

Selective branch formation in ethylene polymerization to access precise ethylene-propylene copolymers

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1. Computational Details

In present work, all quantum chemical computations were performed by using the Gaussian16 package of programs. Each optimized structure was optimized at GGA BP862-4/BSI level, and was subsequently characterized as a minimum (Nimag = 0) or a transition state (Nimag = 1) by harmonic vibration frequencies which providing thermodynamic data. The transition state structures are shown to connect the reactant and product on either side via intrinsic reaction coordinate (IRC) following. In the BSI, the C and H atoms in gray part (Supplementary Figure 1) were considered by 3-21G basis set, the other C, H, O, and N atoms were calculated by the 6-31G* basis set, and the Ni and Pd atoms were treated by the quasi-relativistic LANL2DZ ECP effective core potential. To obtain more reliable relative energies, the single-point calculations of optimized structures were carried out at the level of BP86-D3 (BP86 with Grimme’s DFT-D3 correction)6,7/BSI, taking into account solvation effect of toluene with the SMD8 solvation model. In BSI, the 6-311G(d, p) basis set was used for C, H, O, and N atoms and the Ni and Pd atoms were treated by the Stuttgart/Dresden effective core potential (ECP) and the associated basis sets. Therefore, unless otherwise mentioned, the free energy (ΔG, 298.15 K, 1 atm) in solution, which was used for description of energy profiles, was obtained from the solvation single-point calculation and the gas-phase Gibbs free energy correction. In energy decomposition analysis (EDA), the energies of two fragments, viz., the monomer moiety (A) and the remaining metal complex (B), in the TS geometries were evaluated via single-point calculations. Such single-point energies of the fragments and the energy of TS were used to estimate the interaction energy ΔEint. These energies, together with the energies of the respective fragments in their optimal geometry, allow for the estimation of the deformation energies of the two fragments, ΔEdef(A) and ΔEdef(B). As the energy of the TS, ΔETS, is evaluated with respect to the energy of the two separated fragments, the relation ΔETS = ΔEint + ΔEdef(A) + ΔEdef(B) holds.

2. Detailed Discussion on Mechanisms of Nickel and Palladium System

Nickel system. The intriguing branching character stimulated us to study the related mechanism of ethylene polymerization by nickel species ipty-Ni and palladium species ipty-Pd through using DFT calculations (Supplementary Figures 2 and 3). At first, the reaction starts from the β-H elimination (BHE) based on a β-agostic species 1β-T to give a propylene-coordinated complex 1. This process, which overcomes a free energy barrier (TS1BHE) of 12.9 kcal mol⁻¹, is endergonic by 9.5 kcal mol⁻¹. This unstable 1 goes through a slightly lower TS12reins with an energy barrier of 12.0 kcal mol⁻¹ to complete propylene re-insertion with a 2,1-manner, generating a new β-agostic intermediate 2. By comparison, 2 is the more both kinetically and thermodynamically favorable than 1β-T. Therefore, a new ethylene coordination separating β-agostic-H based on 2 is considered, and is found to be feasible via an energy barrier of 12.7 kcal mol⁻¹, leading to 3. Finally, an ethylene insertion into the Ni–isopropyl bond of 3 occurs via a TS34ins with an energy barrier of 10.0 kcal mol⁻¹ to generate a methyl-branching 4, accompanied with an energy release of 15.1 kcal mol⁻¹. Starting from 4, two possible pathways, viz., the direct ethylene coordination–insertion (4→TS45coor→5→TS56ins→6) and the BHE–2,1-reinsertion (4→TS5BHE→5BHE→C→TS5reins→6reins), were calculated. The former pathway has a total energy barrier of 14.2 (ΔG1β, -3.4→(-17.6), TS45coor) kcal mol⁻¹ and is exergonic by 11.4 (-29.0→(-17.6)) kcal mol⁻¹. By contrast, a higher energy barrier of 18.1 (ΔG2β, 0.5→(-17.6), TS56reins) kcal mol⁻¹ and an endergonic character (5.0 = -12.6→(-17.6), 6reins) in the latter case suggest that 1,2-Me2 unit (6reins) is inaccessible in both kinetics and thermodynamics,
which is in line with the experimental observation. To gain more insight on above difference, the geometries of TS$_{45\text{coor}}$ and TS$_{56\text{reins}}$ are carefully compared as shown in Supplementary Figure 4. In comparison with IP$_{\text{T}}$ and TS$_{45\text{coor}}$, 2,1-reinsertion of 3-methyl-1-butene (MB) in TS$_{56\text{reins}}$ results in the bigger repulsion to phenyls of the auxiliary ligand as suggested by the bigger dihedral angles (119°–125° vs 118°–119° in IP$_{\text{T}}$ and 118°–122° in TS$_{45\text{coor}}$). In addition, the C=C bond of MB deviates from the plane of the Ni-involved ring, which could make MB insertion with a 2,1-mode into Ni–H bond more difficult. Subsequent ethylene insertion into 6$_{\text{reins}}$ (6$_{\text{reins}}$→TS$_{67\text{coor}}$→7→TS$_{878\text{reins}}$→8) has a higher energy barrier of 21.9 (ΔG$_{1}^{‡}$, 4.3 (−17.6). TS$_{67\text{coor}}$) kcal mol$^{-1}$, further confirming that the reverse reaction of 1,2-Me$_2$ unit formation more easily occurs.

To further theoretically access the origin of selectivity on exclusive methyl branches, that is why 1,4-Me$_2$ unit can be produced but longer-chain branch units such as 1,3-Me/Et unit are unavailable, we also investigated further ethylene insertion and BHE based on 6. As indicated in Supplementary Figure 2, the direct ethylene coordination-insertion overcomes a total energy barrier of 13.1 (ΔG$_{1}^{‡}$, -15.9 (−29.0), TS$_{78\text{coor}}$) kcal mol$^{-1}$ and releases an energy of 12.4 (-41.4 (−29.0)) kcal mol$^{-1}$, yielding a precursor (8) of 1,x-Me$_2$ units (x = 2n+4, n = 1, 2, 3, ...). To obtain 1,4-Me$_2$ unit and 1,3-Me/Et unit, a BHE and 2,1-reinsertion from 6 was calculated. Notably, locating 5-methyl-1-hexene-coordinated intermediate 7$_{\text{BHE-C}}$ is fruitless, and just one transition state TS$_{78\text{reins}}$ with an energy barrier of 13.9 (ΔG$_{1}^{‡}$, -15.1 (−29.0)) kcal mol$^{-1}$ is obtained between 6 and 8$_{\text{reins}}$ (1,4-Me$_2$ unit, observed in the experiment). And the relaxed scans (Supplementary Figures 5 and 6) on C2–H1 distance and dihedral angle $\angle$H1-Ni-C2-C1 from TS$_{78\text{reins}}$ to 6 direction indicate that neither a maximum nor a minimum point is found, thus further confirming our results. Then, 8$_{\text{reins}}$ isomerizes to a more stable 8$_{\text{reins-iso}}$ (also 1,4-Me$_2$ unit). It is noteworthy that the generations of 1,6-Me$_2$ unit precursor (ΔG$_{1}^{‡}$ = 13.1 kcal mol$^{-1}$) and 1,4-Me$_2$ unit (ΔG$_{1}^{‡}$ = 13.9 kcal mol$^{-1}$) indicate the similar energy barriers, suggesting that they both can be obtained. This shows a good agreement with experimental results.

Furthermore, in following BHE and reinsertion from 8$_{\text{reins-iso}}$ to 9$_{\text{reins}}$ (1,3-Me/Et unit), we cannot also locate 5-methyl-2-hexene (MH)-coordinated intermediate 8$_{\text{BHE-C}}$ and just obtain one transition state TS$_{88\text{BHE}}$. It is also further confirmed by the relaxed scan (Supplementary Figure 7) on the dihedral angle $\angle$H1-Ni-C2-C1 from 8$_{\text{reins-iso}}$ to 9$_{\text{reins}}$. Unlike 1,4-Me$_2$ unit, the formation of 1,3-Me/Et unit needs going through a higher TS$_{88\text{BHE}}$ with an energy barrier of 24.3 (ΔG$_{1}^{‡}$, -9.0 (−33.3)) kcal mol$^{-1}$ and is an apparently unfavorable process, which is consistent with experimental findings. To have a better understanding on above differences, the optimized geometries for TS$_{878\text{ins}}$, TS$_{78\text{reins}}$, and TS$_{88\text{BHE}}$ were comparatively analyzed as shown in (Supplementary Figure 8). In TS$_{88\text{BHE}}$, the bigger steric repulsion between MH and phenyl groups, as suggested by the bigger dihedral angles (126/129° vs. 122/121° in TS$_{78\text{ins}}$ and 121/120° in TS$_{78\text{reins}}$), can account for the less stability of TS$_{88\text{BHE}}$ in comparison with TS$_{78\text{ins}}$ and TS$_{78\text{reins}}$.

Beyond those, the possibilities of further polymerization based on 8$_{\text{reins}}$ and 8$_{\text{reins-iso}}$ were also considered. It was found that the ethylene coordination-insertion (8$_{\text{reins}}$→TS$_{89\text{coor}}$→9→TS$_{910\text{ins}}$→10) into 8$_{\text{reins}}$ owns an energy barrier of 10.3 (ΔG$_{1}^{‡}$, -19.4 (−29.7)) kcal mol$^{-1}$ and is exergonic by 14.5 ((−44.2 (−29.7))) kcal mol$^{-1}$, while the process (8$_{\text{reins-iso}}$→TS$_{89\text{coor}}$→9′→TS$_{910\text{ins}}$→10) involving 8$_{\text{reins-iso}}$ overcomes a higher energy barrier of 24.2 (ΔG$_{1}^{‡}$, -9.1 (−33.3)) kcal mol$^{-1}$ and is a less exergonic process (-7.9 = -41.2 (−33.3) kcal mol$^{-1}$). Therefore, the subsequent insertion on basis of 8$_{\text{reins}}$ is smooth. Further energy decomposition (Supplementary Figure 9) indicate that the less stability of TS$_{910\text{ins}}$ can be ascribed to the bigger repulsion of poly(ethylene) chain/ethylene monomer and auxiliary ligand, as suggested by a bigger deformation energy (ΔE$_{\text{def}}$ = ΔE$_{\text{def(A)}}$ + ΔE$_{\text{def(B)}}$ = 77.3 vs. 55.5 kcal mol$^{-1}$ in TS$_{910\text{ins}}$), the bigger dihedral angles ($\angle$α$\beta_{1}$$\gamma_{1}$/ $\angle$α$\beta_{2}$$\gamma_{2}$: 124/123° in TS$_{910\text{ins}}$ vs. 121/122° in TS$_{910\text{ins}}$) and a farther distance($\gamma_{1}$−$\gamma_{2}$ = 8.24 Å in TS$_{910\text{ins}}$ vs. 7.96 Å in TS$_{910\text{ins}}$) between two phenyl centers of ligand. Aforementioned findings allow us to conclude that the unique ancillary ligand forms a suitable channel for an exclusive formation of small methyl branches and a precise
distribution of 1,2n+4-Me₂ units (n = 0, 1, 2, 3...) in highly branched polyethylenes. **Palladium system.** Since ipty-Pd also generated highly branched polyethylenes with exclusive methyl branches and precise branch distribution, the same reaction pathways as those of ipty-Ni were also calculated in palladium mediated ethylene polymerization to investigate the discrepancy of between nickel and palladium species (Supplementary Figure 3). The results indicate that the relative energies of all Pd-involved π-complexes (1, 3, 5, 5BHE-c, 7, 7', 9, and 9') are apparently lower than those in the nickel system. Moreover, the geometric characters of transition states (TS₁BHE, TS₁₂reins, TS₅BHE, TS₅reins, TS₇BHE, TS₇reins, and TS₈BHE, Supplementary Figure 10) involved in the process of branch formation are similar to π mode complexes, thus showing lower relative energies than those of the nickel case. Therefore, the Pd with a bigger ionic radius (0.86 Å) shows a stronger preference for stabilizing π-mode complexes in comparison with the Ni (0.69 Å) counterparts, which is consistent with previous reports. As aforementioned, the formation of 1,2-Me₂ unit (6reins) in the Pd system just overcomes an energy barrier of 9.7 (ΔG₂‡, -6.6–(-16.3)) kcal mol⁻¹ and is endergonic by 2.3 (-14.0–(-16.3)) kcal mol⁻¹. Based on this, further ethylene insertion needs to surmount a TS'₆coor via a higher energy barrier of 17.8 (ΔG₅‡, 1.5–(-16.3)) kcal mol⁻¹ than that (ΔG₁‡, 15.5 kcal mol⁻¹) of direct ethylene coordination-insertion into 4. Hence, the thermodynamic instability (6reins: -14.0 vs 4: -16.3) and the more difficult further insertion of ethylene make it hard for producing 1,2-Me₂ unit. Likewise, on the basis of 6, the BHE-reinsertion (6→TS₇BHE→7BHE-c→TS₇reins→8reins) leading to 1,4-Me₂ unit just has a free energy barrier of 7.3 (ΔG₅‡, -20.7–(-28.0)) kcal mol⁻¹ and subsequent ethylene coordination-insertion from 8reins is accessible (with an energy barrier of ΔG₆‡ = 15.0 kcal mol⁻¹ vs. ΔG₇‡ = 27.3 kcal mol⁻¹ based on 8reins-iso). Beyond that, 8reins-iso comes across a 17.2 kcal mol⁻¹ (ΔG₈‡) energy barrier and is endergonic by 3.5 kcal mol⁻¹ to produce 9reins (1,3-Me/Et unit). These results imply the formation of 1,4-Me₂ unit via an easy isomerization (chain walking, low 7.3 kcal mol⁻¹) and a comparable barrier (15.0 kcal mol⁻¹ to compound 10 vs 15.5 kcal mol⁻¹ to compound 8) of subsequent ethylene insertion. The slightly unfavorable kinetics (+2.2 kcal mol⁻¹) indicates an impossibility of the formation of 1,3-Me/Et unit at low temperature but a possibility at higher temperature. This agrees the presence of longer branches in palladium system at elevated temperatures.
Supplementary Methods

**General Procedures:** All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of nitrogen. All solvents were purified from the MBraun SPS system. NMR spectra for the ligand, complex, and polymers were recorded on a Bruker AV400 (\(^1\)H: 400 MHz, \(^{13}\)C: 100 MHz) or a Bruker AV500 (\(^1\)H: 500 MHz, \(^{13}\)C: 125 MHz). NMR assignments were confirmed by \(^1\)H–\(^1\)H COSY experiments when necessary. The molecular weights (\(M_n\)) and molecular weight distributions (\(M_w/M_n\)) of polyethylenes and copolymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220-type high-temperature chromatograph equipped with three PL-gel 10 \(\mu\)m Mixed-B LS type columns at 150 °C. Melting temperature (\(T_m\)) of copolymers were measured through DSC analyses, which were carried out on a Mettler TOPEM TM DSC Instruments under nitrogen atmosphere at heating and cooling rates of 10 °C/min (temperature range: -100–160 °C). Elemental analysis were performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry.

**X-Ray diffraction:** Data collections were performed at −100 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Cu K\(\alpha\) radiation (\(\lambda = 1.54178\) Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package.\(^{11}\) The raw frame data were processed using SAINT and SADABS to yield the reflection data file.\(^{12}\) All structures were solved and refined by full-matrix least-squares procedures on \(F^2\) using SHELXTL or Olex2.\(^{13}\) Refinement was performed on \(F^2\) anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

**Exceptions and special features:** For ipty-Ni, the program SQUEEZE\(^{14}\) was used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecules.

**Explanations of B level alerts on ipty-Ni single crystal structure:** The “THETM01 ALERT 3 B” and “PLAT413 ALERT 2 B” alerts are generated due to that the quality of this single crystal is not very good and there is a large amount of H atom disorder in the structure. We tried to recollect the data from a crystal of higher quality, but attempts to obtain good crystals by using various available solvent systems were failed. The used data was collected from the best crystal that we obtained. We ensured that the two alerts do not affect the structure and the analyzed data was correct.

**Materials:** \(\alpha\)-diimine ligand was prepared using the literature procedure.\(^{15}\)
Preparation of Catalyst

Preparation of pentiptycene aminoanisole: To a solution of pentiptycene aminophenol (3 g, 6.5 mmol) in 100 mL dry DMF at r.t. was added NaH (468 mg, 19.5 mmol) under nitrogen. The mixture foamed and was warmed. CH₃I (0.6 mL, 9.75 mmol) was added after the bubbling ceased and the mixture was stirred at r.t. for 24 h. The reaction was quenched by adding 400 mL of distilled water and the aqueous layer was extracted with 3 × 50 mL of CH₂Cl₂. The combined organic phases were washed with 3 ×50 mL of distilled water and 50 mL of brine. Then the organic phase was separated and dried with sodium sulfate. After evaporation of the solvent the pure product was obtained as white solid (2.6 g, 84.1% yield). This method was similar to our previous study.¹⁵

¹H NMR (500 MHz, 298 K, CDCl₃, 7.26 ppm): δ =7.27-7.36 (m, 8H, aryl-H), 6.98-6.88 (m, 8H, aryl-H), 5.67 (s, 2H, CΗPh₂), 5.39 (s, 2H, CΗPh₂), 3.85 (s, 3H, OCH₃) ppm.

Elemental analysis: Anal. Calcd for C₃₅H₂₅NO: C, 88.39; H, 5.30; N, 2.95. Found: C, 88.16; H, 5.27; N, 2.90.

Preparation of Ligand: A solution of 9,10-dihydro-9,10-ethanoanthracene-11,12-dione (500 mg, 2.12 mmol), pentiptycene aminoanisole (2.5 g, 5.29 mmol) and p-toluenesulfonic acid (5 mg) in toluene (100 mL) was refluxed with Dean-stark trap for 3 days, the solvent was partially evaporated under reduced pressure until the formation of a yellow solid, and the remaining solution was diluted in ethanol (300 mL). The yellow solid was isolated by filtration, washed three times by 20 mL ethanol and dried under high vacuum (1.46 g, 60.2% yield). This method was similar to our previous study.¹⁵

¹H NMR (500 MHz, 298 K, DMSO-d₆, 2.50 ppm): δ =7.65-7.55 (m, 4H, aryl-H), 7.40-7.50 (m, 8H, aryl-H), 7.31-7.26 (m, 4H, aryl-H), 7.25-7.19 (m, 4H, aryl-H), 7.16-7.10 (m, 8H, aryl-H), 7.08-7.00 (m, 4H, aryl-H), 6.99-6.89 (m, 8H, aryl- H), 5.94 (s, 4H, CΗPh₂), 5.11 (s, 4H, CΗPh₂), 5.09 (s, 2H, CΗPh₂), 4.01 (s, 6H, OCH₃) ppm.

Elemental analysis: Anal. Calcd for C₈₆H₅₆N₂O₂: C, 89.87; H, 4.91; N, 2.44. Found: C, 89.99; H, 4.97; N, 2.36.
**Preparation of ipty-Ni:** To a solution of ligand which was reported by us previously (200 mg, 0.174 mmol) in dry dichloromethane (25 mL) was added 53.8 mg (0.174 mmol) of NiBr$_2$(DME) (DME = 1,2-dimethoxyethane). After stirring the mixture for 3 days at room temperature, the solvent was evaporated under reduced pressure, the desired compound could be isolated from repeatedly recrystallized from n-hexane and dichloromethane. The pure compound was obtained as an orange solid. (190 mg, 79.8% yield)

**MALDI-TOF-MS** (m/z): 1285.29 [M-Br] $^+$

**Elemental analysis:** Anal. Calcd for C$_{86}$H$_{56}$Br$_2$N$_2$NiO$_2$: C, 75.51; H, 4.13; N, 2.05. Found: C, 75.80; H, 4.18; N, 2.00.

**General Procedure for the Polymerization**

**A general procedure for ethylene polymerization using Ni catalyst**
In a typical experiment, a 350 mL glass pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 98 mL of toluene and co-catalyst was added to the reactor under N$_2$ atmosphere, then the desired amount of Ni catalyst in 2 mL of CH$_2$Cl$_2$ was injected into the polymerization system via syringe. With a rapid stirring, the reactor was pressurized and maintained at specified pressure of ethylene. After the specified time, the pressure reactor was vented and the polymerization was quenched via the addition of 100 mL acidic EtOH (5% HCl in EtOH) and dried in a vacuum oven to constant weight.
### Supplementary Tables

**Supplementary Table 1. Study on the time effect of ethylene polymerization with ipty-Ni**

| entry | $T$ ($^\circ$C) | $T$ (min) | yield (g) | act. ($10^6$)\(^a\) |
|-------|----------------|-----------|-----------|-----------------------|
| 1     | 30             | 5         | 0.11      | 1.32                  |
| 2     | 30             | 10        | 0.34      | 2.04                  |
| 3     | 30             | 20        | 0.90      | 2.70                  |
| 4     | 30             | 30        | 1.24      | 2.48                  |
| 5     | 30             | 45        | 2.05      | 2.73                  |
| 6     | 90             | 5         | 0.16      | 1.92                  |
| 7     | 90             | 10        | 0.43      | 2.58                  |
| 8     | 90             | 20        | 0.51      | 1.53                  |
| 9     | 90             | 30        | 0.60      | 1.20                  |

\(^a\) Reaction conditions: ipty-Ni catalyst (1 $\mu$mol), MMAO (500 eq.), toluene/CH\(_2\)Cl\(_2\) (98 mL/2 mL), ethylene pressure (8 bar), all entries are based on at least two runs, unless noted otherwise. \(^b\) Activity is in unit of g mol\(^{-1}\) h\(^{-1}\).

**Supplementary Table 2. Crystallographic data for ipty-Ni**

| ipty-Ni | C\(_{86}\)H\(_{56}\)Br\(_2\)N\(_2\)NiO\(_2\) |
|---------|------------------------------------------|
| Formula | 1367.85                                   |
| Formula weight |                         | 0.30 $\times$ 0.28 $\times$ 0.20 |
| Crystal dimensions (mm\(^3\))  | monochinic                |
| Crystal system |                                 |
| Space group | P 1 21/m 1                           |
| a (Å)   | 12.5340(14)                             |
| b (Å)   | 19.232(2)                               |
| c (Å)   | 16.085(2)                               |
| $\alpha$ (º) | 90                                      |
| $\beta$ (º) | 111.704(8)                            |
| $\gamma$ (º) | 90                                    |
| Volume (Å\(^3\)) | 3602.5(8)                           |
| Z       | 2                                        |
| $T$ (K) | 173(2)                                   |
| $D_{calc}$ (g cm\(^{-3}\)) | 1.261                                 |
| $\mu$ (mm\(^{-1}\)) | 2.059                             |
| $F$ (000) | 1400                               |
| No. of reflns. collected | 17682                                 |
| No. of indep. reflns. /$R_{int}$ | 5244 / 0.1321                        |
| No. of obsd. reflns. [$I_o > 2\sigma(I_o)$] | 3448                                |
| Data / restraints / parameters | 5244 / 0 / 424                     |
| $R_I$ / $wR_2$ [$I_o > 2\sigma(I_o)$] | 0.0837 / 0.1818                   |
| $R_I$ / $wR_2$ (all data) | 0.1173 / 0.1992                        |
| GOF (on $F^2$) | 1.138                        |
| Largest diff. peak and hole (e Å\(^{-3}\)) | 1.186 / -0.619                  |
| CCDC No. | 1974098                             |
Supplementary Figures

**Supplementary Figure 1.** The structure of complex $1_{\beta-T}$. 

$M = \text{Ni, Pd}$
Supplementary Figure 2. Mechanism for the Formation of Branch Generated by ipty-Ni from the DFT simulation.
Supplementary Figure 3. Mechanism for the Formation of Branch Generated by ipty-Pd from the DFT simulation.
**Supplementary Figure 4.** Optimized geometrics (dihedral angles in degree) of $\mathbf{1}_{\beta-T}$, $\mathbf{TS}_{45\text{coor}}$, and $\mathbf{TS}_{56\text{reins}}$.

**Supplementary Figure 5.** Relaxed scan of potential energy surface (PES) for the distance (angstrom) of C2 and H1 and dihedral angle (degree) $\angle \text{H1-Ni-C2-C1}$ in $\mathbf{TS}_{78\text{reins}}$ at the DFT/BSI level. We can observe that the dihedral angle (degree) $\angle \text{H1-Ni-C2-C1}$ in $\mathbf{TS}_{78\text{reins}}$ is about 60° and the $\mathbf{TS}_{78\text{reins}}$ from its’ geometry is very near to $\mathbf{8}_{\text{reins}}$. So we just scan the distance of C2 and H1 and dihedral angle $\angle \text{H1-Ni-C2-C1}$ in $\mathbf{TS}_{78\text{reins}}$ to the direction of $\mathbf{6}$, and no other transition state and intermediate are found. In addition, we also confirm that all transition state structures are shown to connect the reactant and product on either side via intrinsic reaction coordinate (IRC) following. For example, the structure $\mathbf{TS}_{78\text{reins}}$ definitely connecting the reactant $\mathbf{6}$ and product $\mathbf{8}_{\text{reins}}$ is verified as shown in next Supplementary Figure 6.
Supplementary Figure 6. IRC analysis for TS_{7reins} and optimized processes of the 6 and 8_{reins}.

Supplementary Figure 7. Relaxed scan of potential energy surface (PES) for the dihedral angle (degree) $\angle$H1-Ni-C2-C1 and the optimization process of 9_{reins} starting from A at the DFT/BSI level. For exploring the reaction pathway from of 8_{reins-iso} and 9_{reins}, we scan the dihedral angle (degree) $\angle$H1-Ni-C2-C1 and just one peak point is found. The optimized results confirm that the peak point B and the A point are optimized to give TS_{8BHE} and 9_{reins}, respectively.
Supplementary Figure 8. Optimized geometrics (dihedral angles in degree) of TS78ins, TS78reins, and TSBBHE. The optimized geometrics for TS78ins, TS78reins, and TSBBHE was comparatively analyzed. In TSBBHE, the bigger steric repulsion between MH and phenyl groups, as suggested by the bigger dihedral angles (126/129° vs. 122/121° in TS78ins and 121/120° in TS78reins), could account for the less stability of TSBBHE in comparison with TS78ins and TS78reins.

Supplementary Figure 9. Energy decomposition ($\Delta E$ in kcal mol$^{-1}$) and geometrical analyses (dihedral angles in degree and distance in Å) for TS910ins and TS'910ins. Further energy decomposition and structural analyses indicate that the less stability of TS910ins could be ascribed to the bigger repulsion of poly(ethylene) chain/ethylene monomer and auxiliary ligand, as suggested by a bigger deformation energy ($\Delta E_{\text{def}} = \Delta E_{\text{def(A)}} + \Delta E_{\text{def(B)}} = 77.3$ vs. 55.5 kcal mol$^{-1}$ in TS910ins), the bigger dihedral angles ($\angle \alpha_1 \beta_1 \gamma_1 / \angle \alpha_1 \beta_2 \gamma_2$: 124°/123° vs. 121/122 in TS910ins) and a farther distance ($\gamma_1 - \gamma_2 = 8.24$ vs. 7.96 Å in TS910ins) between two phenyl centers of ligand.
Supplementary Figure 10. Optimized geometrics (distance in Å) involved in branching process of ipty-Pd system.
Supplementary Figure 11. Plots of yield of polyethylenes generated vs. reaction time with ipty-Ni at different temperatures in Supplementary Table 1.

$^1$H, $^{13}$C, $^1$H-$^1$H COSY NMR of ipty-Ni.

Supplementary Figure 12. $^1$H NMR spectrum (298K, CDCl$_3$) of ipty-Ni.
Supplementary Figure 13. $^1$H-$^1$H COSY NMR spectrum (298K, CDCl$_3$) of ipty-Ni.
\[ \text{Branches} = \text{Me groups} / 1000 C = \frac{2 \times I_{Me}}{3 \times I_{tot}} \times 1000 = \frac{2 \times 3}{3 \times (16.86+3)} \times 1000 = 101 \]

**Supplementary Figure 14.** $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by **ipty-Ni** from table 1, entry 1 and table 2, entry 1.

**Supplementary Figure 15.** $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by **ipty-Ni** from table 1, entry 2 and table 2, entry 2.
Supplementary Figure 16. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipty-Ni from table 1, entry 3 and table 2, entry 3.

Supplementary Figure 17. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipty-Ni from table 1, entry 4 and table 2, entry 4.
Supplementary Figure 18. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipy-Ni from table 1, entry 5 and table 2, entry 5.

Supplementary Figure 19. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipy-Ni from table 1, entry 6 and table 2, entry 6.
Supplementary Figure 20. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipty-Ni from table 1, entry 7 and table 2, entry 7.
Supplementary Figure 21. $^{13}$C NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipty-Ni from table 1, entry 1 and table 2, entry 1.
Supplementary Figure 22. $^{13}$C NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipty-Ni from table 1, entry 2 and table 2, entry 2.

Supplementary Figure 23. $^{13}$C NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipty-Ni from table 1, entry 3 and table 2, entry 3.
Supplementary Figure 24. $^{13}$C NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipty-Ni from table 1, entry 4 and table 2, entry 4.

Supplementary Figure 25. $^{13}$C NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipty-Ni from table 1, entry 5 and table 2, entry 5.
**Supplementary Figure 26.** $^{13}$C NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipty-Ni from table 1, entry 6 and table 2, entry 6.

**Supplementary Figure 27.** $^{13}$C NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipty-Ni from table 1, entry 7 and table 2, entry 7.
Supplementary Figure 28. $^{13}$C NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipty-Pd from table 2, entry 8.

Supplementary Figure 29. $^{13}$C NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipty-Pd from table 2, entry 9.
Supplementary Figure 30. $^{13}$C NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipty-Pd from table 2, entry 10.

Supplementary Figure 31. $^{13}$C NMR spectrum (100 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the polyethylene generated by ipty-Ni from table 2, entry 1 to 7.
Supplementary Figure 32. XRD of the polymers generated by complex ipty-Ni from table 2, entry 1 to 4. Among them, partially crystalline polymers were obtained at temperature range of 30 °C to 70 °C.
**GPC of Polymers**

Supplementary Figure 3. GPC trace of the polymer from table 1, entry 1.

**Supplementary Figure 34.** GPC trace of the polymer from table 1, entry 2.
Supplementary Figure 35. GPC trace of the polymer from table 1, entry 3.

Supplementary Figure 36. GPC trace of the polymer from table 1, entry 4.
Supplementary Figure 37. GPC trace of the polymer from table 1, entry 5.

MW Averages
| Peak No | Mp  | Mn  | Mw  | Mz  | Mz+1 | Mv  | PD  |
|---------|-----|-----|-----|-----|------|-----|-----|
| 1       | 541930 | 356112 | 586185 | 842486 | 1113222 | 552884 | 1.64607 |

Processed Peaks
| Peak No | Name    | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV, secs) | % Area |
|---------|---------|-----------------|---------------|---------------|----------------|-----------|-----------------|--------|
| 1       | Concentration | 16.02 | 17.97 | 21.23 | -14.5779 | 0 | 1608 | 100 |
| 2       | LS 15 | 15.87 | 17.57 | 20.73 | 60.9801 | 0 | 6026.53 | 100 |
| 3       | LS 90 | 15.72 | 17.70 | 20.97 | 222.201 | 0 | 21500.4 | 100 |
| 4       | Diff Pressure | 15.80 | 17.70 | 20.55 | 207.833 | 0 | 20875.6 | 100 |

Supplementary Figure 38. GPC trace of the polymer from table 1, entry 6.

MW Averages
| Peak No | Mp  | Mn  | Mw  | Mz  | Mz+1 | Mv  | PD  |
|---------|-----|-----|-----|-----|------|-----|-----|
| 1       | 479553 | 350760 | 526227 | 724559 | 928458 | 500739 | 1.50025 |

Processed Peaks
| Peak No | Name    | Start RT (mins) | Max RT (mins) | End RT (mins) | Pk Height (mV) | % Height | Area (mV, secs) | % Area |
|---------|---------|-----------------|---------------|---------------|----------------|-----------|-----------------|--------|
| 1       | Concentration | 16.42 | 18.13 | 20.85 | -18.8176 | 0 | 2060.71 | 100 |
| 2       | LS 15 | 16.27 | 17.75 | 20.07 | 70.1476 | 0 | 6976.98 | 100 |
| 3       | LS 90 | 16.30 | 17.83 | 20.28 | 263.917 | 0 | 25851.9 | 100 |
| 4       | Diff Pressure | 16.28 | 17.85 | 20.13 | 246.936 | 0 | 24848.3 | 100 |
Supplementary Figure 39. GPC trace of the polymer from table 1, entry 7.
DSC of Polymers

Supplementary Figure 40. DSC data of the polymer from table 2, entry 1.

Supplementary Figure 41. DSC data of the polymer from table 2, entry 2.
**Supplementary Figure 42.** DSC data of the polymer from table 2, entry 3.

**Supplementary Figure 43.** DSC data of the polymer from table 2, entry 4.
Supplementary Figure 44. DSC data of the polymer from table 2, entry 5.

Supplementary Figure 45. DSC data of the polymer from table 2, entry 6.
Supplementary Figure 46. DSC data of the polymer from table 2, entry 7.
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