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# Facile Synthesis of Hyperbranched Ethylene Oligomers and Ethylene/Methyl Acrylate Co-oligomers with Different Microscopic Chain Architectures

Huijun Fan,[||] Guanru Chang,[||] Huiqin Bi, Xu Gui, Hui Wang,* Guoyong Xu,* and Shengyu Dai*

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**ABSTRACT:** Low-molecular-weight (MW) ethylene oligomers with hyper-branched microstructures are often difficult to be synthesized by traditional catalytic processes. In this study, a series of *N*-terphenyl iminopyridyl ligands and the corresponding Pd(II) and Ni(II) complexes bearing remote conjugated substituents with different electronic effects (H, Me, F, Cl, and *t*Bu) were synthesized in a simple and efficient way. These Pd(II) and Ni(II) complexes were highly effective in the ethylene oligomerization and co-oligomerization with methyl acrylate (MA). Low-MW ethylene oligomers with hyperbranched microstructures were generated using the iminopyridyl Pd(II) and Ni(II) complexes in ethylene oligomerization. More importantly, polar functionalized ethylene−MA co-oligomers with low MWs and varying incorporation ratios were generated via ethylene and MA co-oligomerization using the Pd(II) complexes. Most notably, these ethylene oligomers obtained by different metal species showed a significant

difference in microscopic chain architectures. The remote conjugated electron effect showed little effect on the polymerization parameters of the iminopyridyl system, which is very different from those of the salicylaldiminato system.

**KEYWORDS:** *N*-terphenyl iminopyridyl ligands, Ni(II) and Pd(II) complexes, hyperbranched ethylene oligomers, ethylene−MA co-oligomers
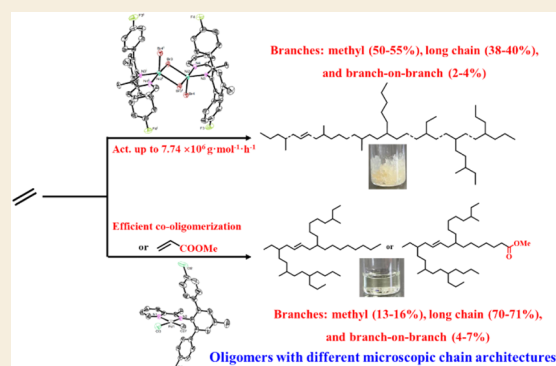
## 1. INTRODUCTION

Low-molecular-weight (MW) ethylene oligomers with hyper-branched microstructures are often difficult to be synthesized by traditional catalytic processes, and they may be employed as functional additives in surface modifiers or lubricants.[1] The key to the preparation of these hyperbranched materials is the selection of catalysts. These catalysts are required to have strong chain walking and chain transfer ability in ethylene oligomerization concurrently.[1] Considering the above require-ments, the known functionality of late-transition-metal catalysts, such as neutral N,O-salicylaldiminato Ni(II)[1−4] and cationic Ni(II)- and Pd(II)-α-diimine catalysts,[5−7] may be particularly important. For example, Mecking et al.[1] reported that low-MW hyperbranched ethylene oligomers were accessible by ethylene oligomerization reactions with Ni(II)-salicylaldiminato catalysts (Scheme 1a). *N*-Terphenyl motifs with remote alkyl substituents may favor the formation of these highly branched oligomers. Unfortunately, the catalyst is not able to directly catalyze the copolymerization of ethylene and vinyl polar monomers. Milani et al. successfully used the less bulky, unsymmetrical bis(aryl-imino) acenaphthene Pd(II) catalysts (Scheme 1b)[6] to produce hyperbranched ethylene oligomers and ethylene/methyl acrylate (MA) co-oligomers with a high incorporation ratio (~14.7 mol %). However, due

to the easy rotation of C=N−Ar without hindrance by the bulky o-aryl substituents, the catalytic activity and stability could not be endured during the polymerization process. Recently, hyperbranched ethylene oligomers were successfully obtained using the benzyl Ni(II) complexes of 5-aryl-2-iminopyrrolyl ligands (Scheme 1c) in ethylene polymerization conducted by Gomes et al.[8] In this case, the highly branched microstructures (100−115/1000 C) were characterized with random distribution of methyl (40−60%) and longer branches (≥C4, 30−40%), including the *sec*-butyl branches.

The common feature of the above systems is that there is only one-side steric hindrance in the axial direction of the metal centers. The iminopyridyl Pd(II) and Ni(II) complexes also display only one steric hindrance in the axial location (Chart 1). In addition to the α-diimine systems, a number of bidentate [N,N] iminopyridine ligands have been reported
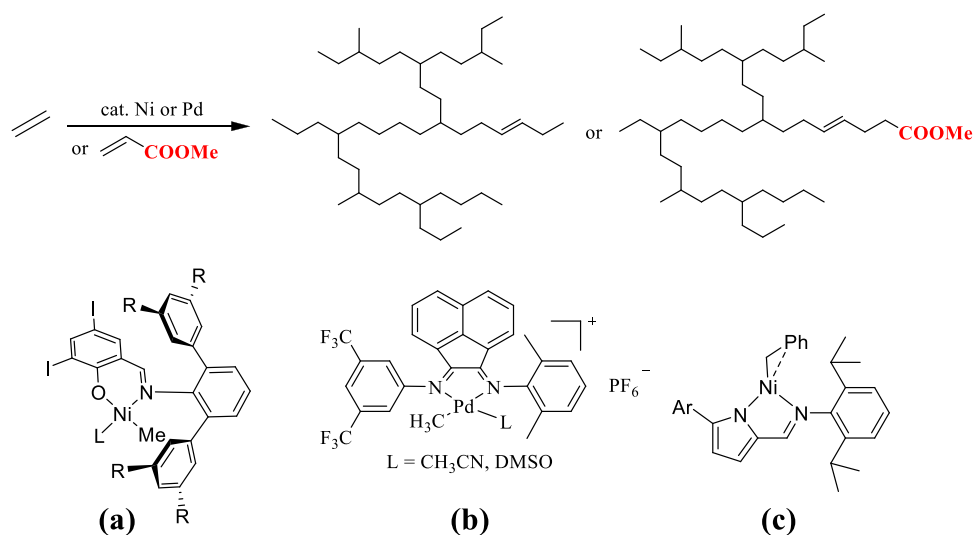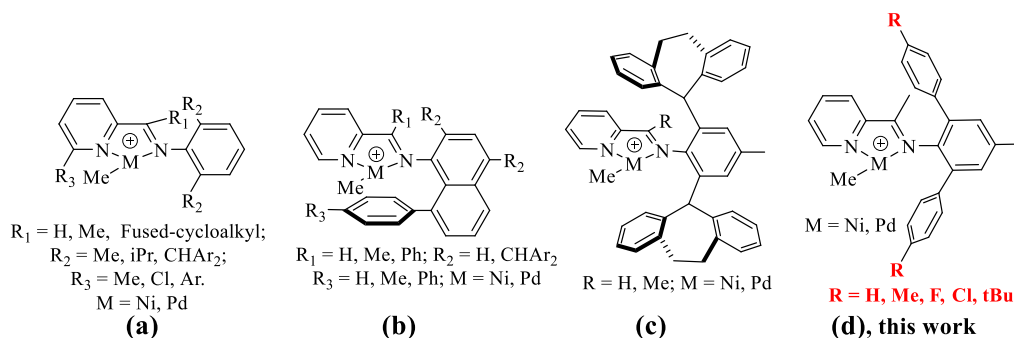
**Scheme 1. Representative Ni(II) and Pd(II) Catalysts for the Synthesis of Hyperbranched Ethylene Oligomers or Ethylene–MA Co-oligomers**



**Chart 1. Typical Iminopyridyl Pd(II) and Ni(II) Catalysts (a–c) and Our Current Work (d)**



$R_1$ = H, Me, Fused-cycloalkyl;
$R_2$ = Me, iPr, CHAr$_2$;
$R_3$ = Me, Cl, Ar.
M = Ni, Pd
**(a)**

$R_1$ = H, Me, Ph; $R_2$ = H, CHAr$_2$
$R_3$ = H, Me, Ph; M = Ni, Pd
**(b)**

R = H, Me; M = Ni, Pd
**(c)**

M = Ni, Pd

R = H, Me, F, Cl, tBu
**(d), this work**

**Scheme 2. Synthesis of Iminopyridine Ligands and the Corresponding Iminopyridyl Ni(II) and Pd(II) Complexes**



**R = H (Ni1 or Pd1), Me (Ni2 or Pd2), F (Ni3 or Pd3), Cl (Ni4 or Pd4), tBu (Ni5 or Pd5)**
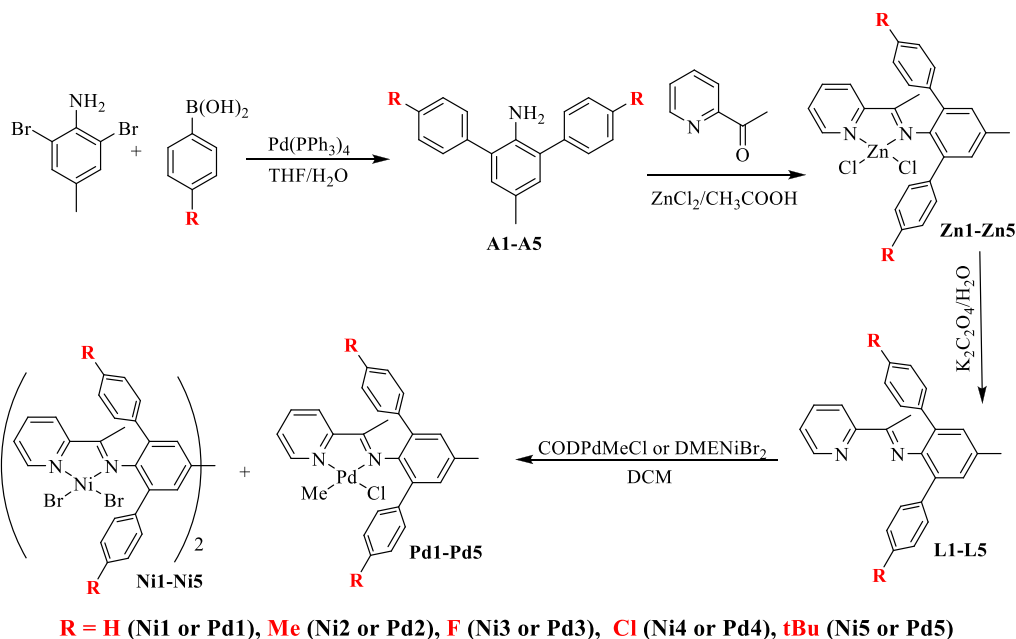
(Chart 1).[9] The first example of ethylene polymerization using an iminopyridine Ni(II) catalyst was reported by Laine et al.[10] in 1999 (Chart 1a). After that, Sun, Jian, Gao, Kress, Daugulis,

and Brookhart et al.[9−24] modified the iminopyridyl systems, mainly through the introduction of ortho-aryl bulky substituents, modification of the pyridine backbone, and
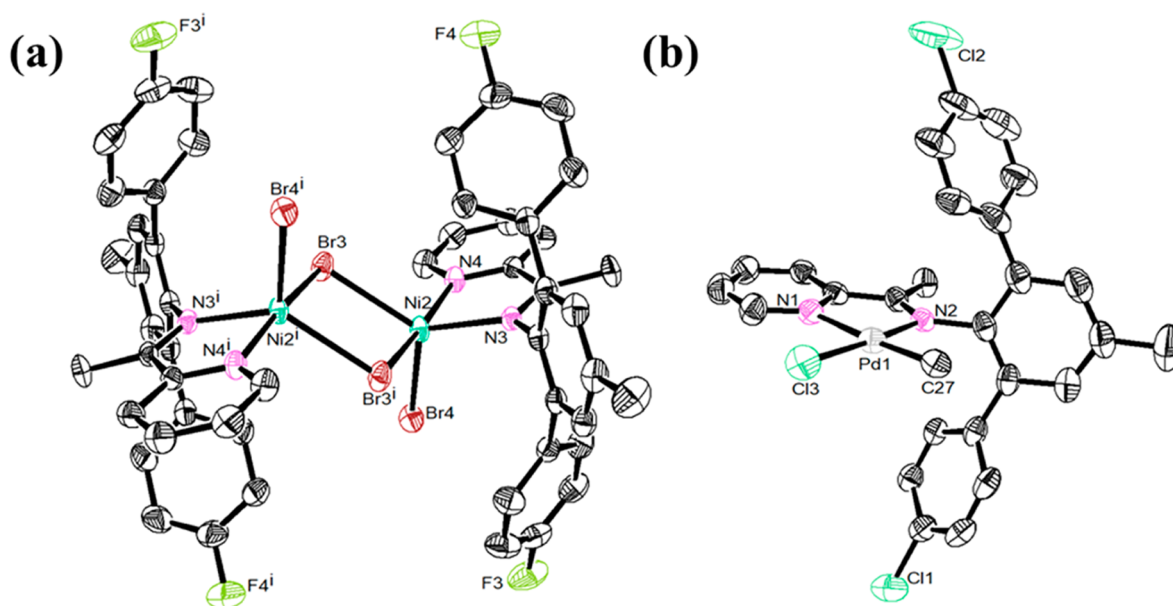
**Figure 1.** Solid-state molecular structures of **Ni3** (2109732) and **Pd4** (2109733) at the 30% probability level. All solvent molecules and hydrogen atoms are omitted for better clarity.

regulation of electronic effects (Chart 1a). These iminopyridyl Pd(II) and Ni(II) catalysts generally yield highly branched polymers with low-to-moderate MWs.[25] Recently, we have developed a series of palladium and nickel catalysts with a half "sandwich" 8-aryl-naphthyl substituent or rotation-restricted dibenzosuberyl groups, which can catalyze ethylene polymerization to yield high-MW polyethylene.[25−28] More importantly, the corresponding palladium catalysts allow the production of the polar functionalized polyethylene with a high MW and incorporation ratio (~24 mol %) (Chart 1b,c).[29] Pellecchia and Milani et al.[30,31] used the iminopyridyl Ni(II) catalysts with bulky substituents in the 6-position of pyridine to generate hyperbranched ethylene oligomers and polar functional ethylene oligomers in ethylene (co)oligomerization. However, the existence of 6-position substituents greatly affects the coordination−insertion of ethylene, thus resulting in the low polymerization and copolymerization activity of the system.

In this study, we designed and synthesized a series of *N*-terphenyl iminopyridyl Pd(II) and Ni(II) complexes (Chart 1d), inspired by Mecking's Ni(II)-salicylaldiminato catalysts (Scheme 1a). These Pd(II) and Ni(II) complexes were highly effective in the ethylene oligomerization and co-oligomerization with MA for preparing hyperbranched ethylene oligomers and ethylene/MA co-oligomers.

## 2. RESULTS AND DISCUSSION

### 2.1. Synthesis and Characterization of Iminopyridyl Ni(II) and Pd(II) Complexes

Terphenyl amines **A1−A5** containing remote substituents with different electronic effects were synthesized via the Suzuki coupling reaction of 4-substituted phenylboronic acid and 2,6-dibromo-4-methylaniline. Condensation with 2-acetylpyridine using the template-type method afforded the iminopyridine ligands **L1−L5**, which involved the zinc template complex synthesis and the removal of zinc chloride (Scheme 2).[32,33] The ligands were obtained in high yields (70−80%) with no chromatography involved and characterized by using $^{1}$H, $^{13}$C,

**Table 1. Ethylene Oligomerization with Ni(II) Catalysts**[a]

| Ent. | Precat. | $T$/°C | yield/g | Act.[b] | $M_n$ (NMR)[c] | $M_n$[d] | $M_w/M_n$[d] | $B$[e] |
|---|---|---|---|---|---|---|---|---|
| 1 | **Ni1** | 30 | 0.92 | 5.52 | 2.8 | 2.2 | 1.41 | 66 |
| 2 | **Ni1** | 50 | 1.17 | 7.02 | 2.4 | 2.1 | 1.42 | 67 |
| 3 | **Ni1** | 70 | 1.12 | 6.72 | 1.6 | 1.7 | 1.36 | 68 |
| 4 | **Ni2** | 30 | 1.14 | 6.84 | 2.6 | 2.4 | 1.41 | 65 |
| 5 | **Ni2** | 50 | 1.21 | 7.26 | 2.0 | 2.0 | 1.42 | 68 |
| 6 | **Ni2** | 70 | 1.05 | 6.30 | 1.7 | 1.9 | 1.35 | 71 |
| 7 | **Ni3** | 30 | 1.02 | 6.12 | 2.6 | 2.4 | 1.42 | 59 |
| 8 | **Ni3** | 50 | 1.14 | 6.84 | 2.1 | 2.1 | 1.43 | 62 |
| 9 | **Ni3** | 70 | 1.04 | 6.24 | 1.5 | 1.7 | 1.36 | 65 |
| 10 | **Ni4** | 30 | 1.08 | 6.48 | 1.6 | 1.5 | 1.46 | 54 |
| 11 | **Ni4** | 50 | 1.15 | 6.90 | 1.4 | 1.4 | 1.45 | 62 |
| 12 | **Ni4** | 70 | 1.14 | 6.84 | 1.4 | 1.2 | 1.36 | 63 |
| 13 | **Ni5** | 30 | 0.99 | 5.94 | 1.6 | 2.2 | 1.40 | 57 |
| 14 | **Ni5** | 50 | 1.29 | 7.74 | 1.0 | 1.8 | 1.43 | 61 |
| 15 | **Ni5** | 70 | 1.01 | 6.06 | 0.9 | 1.4 | 1.32 | 70 |

[a]Conditions: Ni(II) complexes (1 μmol, calculated by the number of nickel metal centers), 500 equiv of Et$_2$AlCl, 1 mL of CH$_2$Cl$_2$, 20 mL of toluene, polymerization time (10 min), 6 atm. [b]Activity (Act.) = $10^6$ g/(mol Ni·h). [c]$M_n$ (NMR) (kg mol$^{-1}$) calculated from the $^{1}$H NMR intensity ratio of unsaturated end groups vs the overall integral. [d]$M_n$ is in units of kg mol$^{-1}$, determined by GPC in THF at 40 °C. [e]$B$ = branches per 1000 carbons, determined by $^{1}$H NMR spectroscopy, $B = 1000 \times 2(I_{CH_3})/3(I_{CH_2+CH} + I_{CH_3})$, corrected for saturated end groups.

$^{19}$F NMR (Figures S3−S13), and mass spectroscopy (Figures S26−S30). The reaction with 1.0 equiv of dimethoxyethane NiBr$_2$ in dichloromethane at ambient temperature yielded Ni(II) complexes **Ni1−Ni5** in excellent yields (84−94%) (Scheme 2). The purity and identity of **Ni1−Ni5** were examined by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) (Figures S31−S35) and elemental analysis. Similarly, the corresponding Pd(II) complexes **Pd1−Pd5** were synthesized by exposing the ligands **L1−L5** to 1,5-cyclooctadiene PdMeCl (Scheme 2) in
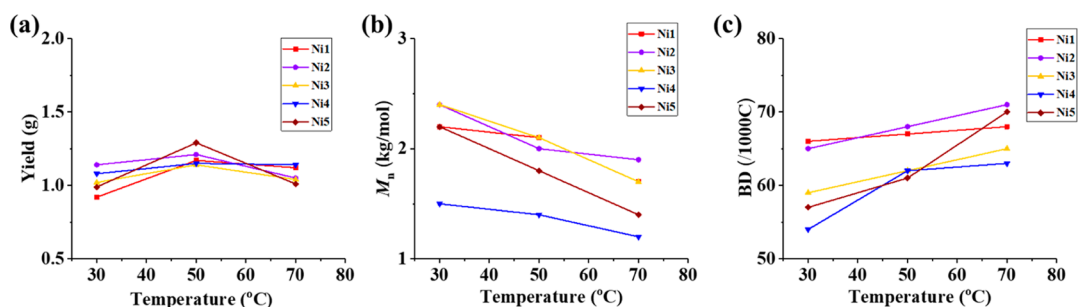
**Figure 2.** Comparisons of yield (a), MW (b), and branching density (c) of ethylene oligomers obtained with catalysts **Ni1−Ni5** at 30−70 °C.
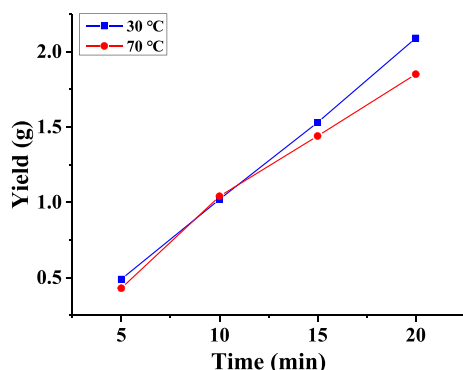


**Figure 3.** Plots of yield vs time for complex **Ni3** at 30 (blue) and 70 (red) °C.

### Table 2. Ethylene Oligomerization with Pd(II) Catalysts[a]

| Ent. | Precat. | $T/°C$ | Yield/g | Act.[b] | $M_{n(NMR)}$[c] | $B$[d] |
|---|---|---|---|---|---|---|
| 1 | **Pd1** | 30 | 0.93 | 3.1 | 519 | 84 |
| 2 | **Pd1** | 50 | 1.54 | 5.1 | 338 | 85 |
| 3 | **Pd2** | 30 | 1.17 | 3.9 | 544 | 89 |
| 4 | **Pd2** | 50 | 1.78 | 5.9 | 260 | 93 |
| 5 | **Pd3** | 30 | 1.44 | 4.8 | 339 | 66 |
| 6 | **Pd3** | 50 | 2.24 | 7.5 | 285 | 71 |
| 7 | **Pd4** | 30 | 1.81 | 6.0 | 382 | 67 |
| 8 | **Pd4** | 50 | 3.51 | 11.7 | 265 | 72 |
| 9 | **Pd5** | 30 | 0.86 | 2.9 | 787 | 97 |
| 10 | **Pd5** | 50 | 1.78 | 5.9 | 355 | 103 |

[a]Reaction conditions: Pd(II) catalyst (10 μmol), NaBArF (2.0 equiv), $CH_2Cl_2$ (40 mL), polymerization time (3 h), ethylene (4 atm). [b]Activity is in units of $10^4$ g mol$^{-1}$ h$^{-1}$. [c]MWs (g mol$^{-1}$) calculated from the $^1$H NMR intensity ratio of unsaturated end groups vs the overall integral. [d]$B = 1000 \times 2(I_{CH_3})/3(I_{CH_2+CH} + I_{CH_3})$, $B$ = branches per 1000 carbons, determined by $^1$H NMR spectroscopy, corrected for saturated end groups.

dichloromethane at ambient temperature. The obtained Pd(II) complexes were verified by $^1$H, $^{13}$C, $^{19}$F NMR, (Figures S14−

### Table 3. Ethylene−MA Co-oligomerization with Pd(II) Catalysts[a]

| Ent. | Precat. | yield (g) | Act.[b] | $X_M$ (mol %)[c] | $M_{n(NMR)}$[d] | $B$[e] |
|---|---|---|---|---|---|---|
| 1 | **Pd1** | 3.78 | 15.75 | 3.86 | 284 | 89 |
| 2 | **Pd2** | 2.81 | 11.70 | 4.41 | 287 | 91 |
| 3 | **Pd3** | 3.93 | 16.38 | 3.28 | 271 | 83 |
| 4 | **Pd4** | 4.72 | 19.67 | 2.61 | 269 | 85 |
| 5 | **Pd5** | 2.75 | 11.46 | 4.92 | 402 | 87 |
| 6[f] | **Pd5** | 1.73 | 7.21 | 9.58 | 435 | 84 |
| 7[g] | **Pd5** | 0.72 | 3.00 | 19.82 | 527 | 89 |

[a]General conditions: Pd(II) catalyst (20 μmol), NaBArF (2.0 equiv), polymerization time (12 h), ethylene (4 atm), total volume of $CH_2Cl_2$ and MA (20 mL), MA (0.5 M), temperature (30 °C). [b]Activity ($10^3$ g mol$^{-1}$ h$^{-1}$). [c]$X_{MA}$ = MA incorporation (mol %). [d]$M_{n\,(NMR)}$ is in units of g mol$^{-1}$, MWs calculated from the $^1$H NMR intensity ratio of unsaturated end groups vs the overall integral. [e]$B$ = Number of branches per 1000 C, as determined by $^1$H NMR spectroscopy. The polar functional branches are added to the total branches, corrected for saturated end groups. [f]MA = 1.0 M. [g]MA = 2.0 M.

S24), MALDI-TOF MS (Figures S36−S40), and elemental analysis.

The single crystals of **Ni3** and **Pd4** were prepared by layering their $CH_2Cl_2$ solution with a diethyl ether−dichloromethane mixture (v/v = 1/1) and pure diethyl ether sequentially (Figure 1). The complex **Ni3** formed as a centrosymmetric dimer structure, in which each nickel atom was bridged by two bromine atoms and one iminopyridine ligand. The square-pyramidal coordination sphere was completed by a terminal bromine atom at the metal center. Meanwhile, the complex **Pd4** crystallized as a monomer and displayed a square-planar geometry at the Pd(II) center. The ortho-aryl groups in both molecular structures oriented away from the metal centers. These findings indicate that the axial shielding performance of the complexes with aryl substituents may be low at the metal centers, which in turn leads to a chain-transfer reaction during polymerization.
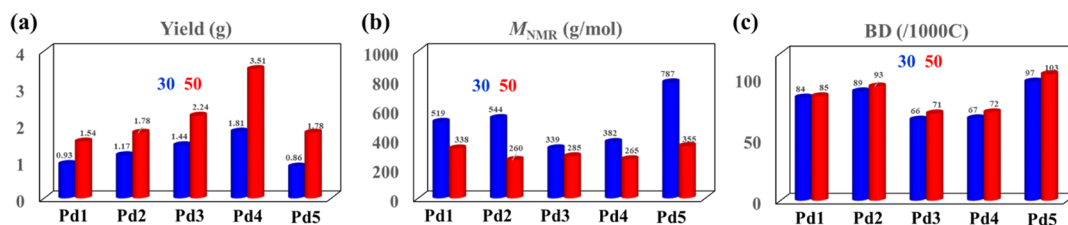


**Figure 4.** Comparisons of yield (a), MW (b), and branching density (c) of ethylene oligomers obtained with catalysts **Pd1−Pd5** at 30 °C (blue) and 50 °C (red).

**Table 4. Microstructure Analysis with Fractional Amounts of Different Branch Lengths[a]**

| Ent. | oligomers | branches/1000 C | methyl[a] (%) | ethyl[a] (%) | propyl[a] (%) | S, C$_{4+}$[a] (%) | sec-butyl[a] (%) |
|---|---|---|---|---|---|---|---|
| 1[b] | **Ni3-30** | 59 | 55 | 2 | 3 | 38 | 2 |
| 2[b] | **Ni3-50** | 62 | 52 | 3 | 3 | 39 | 3 |
| 3[b] | **Ni3-70** | 65 | 50 | 3 | 3 | 40 | 4 |
| 4[c] | **Pd3-30** | 66 | 16 | 8 | 2 | 70 | 4 |
| 5[c] | **Pd3-50** | 71 | 13 | 7 | 2 | 71 | 7 |
| 6[d] | **Pd3-MA** | 83 | 13 | 5 | 2 | 76 | 4 |

[a]Percentages of different branch lengths can be calculated from the relative intensity ratios of the methyl (1B$_1$, 1B$_2$, 1B$_3$, 1B$_n$, S1, and sec-butyl) signals of the respective branches in the $^{13}$C NMR spectra. [b]Ethylene oligomers obtained by using **Ni3** at 30−70 °C (Table 1, entries 7−9). [c]Ethylene oligomers obtained by using **Pd3** at 30 and 50 °C (Table 2, entries 5−6). [d]Ethylene/MA co-oligomer obtained by using **Pd3** at 0.5 M MA (Table 3, entry 3).

## 2.2. Ethylene Oligomerization Catalyzed by Ni(II) Complexes

Following activation with 500 equiv of Et$_2$AlCl, the Ni(II) complexes exhibited very high activities toward ethylene oligomerization (5.52−7.74 × 10$^6$ g·mol$^{-1}$·h$^{-1}$, Table 1). The ethylene oligomers derived from **Ni1−Ni5** demonstrated a low MW (ca. 1−2 kg/mol) and high branching density (54−71/1000 C). All the ethylene oligomers exhibited an oily or waxy form. In general, the oligomerization activity was hardly affected by the catalysts and the reaction temperature, and the oligomerization yields were ca. 1.0 g (Figure 2a). These results show that the remote electron effect of the catalysts and the oligomerization temperature have little effect on the activity, which may be due to the balance of catalyst stability, mass transfer effect, and ethylene solubility with temperature. The plots of yields versus time for complex **Ni3** at 30 and 70 °C are shown in Figure 3 (Table S1). Oligomer productions increased almost linearly versus time over 20 min at both low and high temperatures. These results indicated that complex **Ni3** has good thermal stability toward ethylene oligomerization. As the temperature increased from 30 to 70 °C in the Ni(II) system, the MW of the yielded ethylene oligomers was reduced, while the branching density was elevated (Figure 2b,c). This may be attributed to the increasing ratios of chain transfer-to-the chain growth and chain walking-to-chain growth with increasing temperature.[34−41] Furthermore, the remote electronic effects (H, Me, F, Cl, and tBu) showed little improvement toward the branching density, MW, and catalytic activity of the Ni(II) system, which was different from the previously reported salicylaldiminato nickel system and α-diimine nickel system.[42−45] It should be noted that lowly branched polyethylene with a high MW was obtained using the symmetrical α-diimine nickel catalyst based on similar terphenyl amines, which is contrary to the results of our system.[46−48]

## 2.3. Ethylene (Co)oligomerization Catalyzed by Pd(II) Complexes

All of the iminopyridine Pd(II) complexes were employed as catalytic system components during the ethylene oligomerization process. The oligomerization reactions with complexes **Pd1−Pd5** were performed after adding 2 equiv of sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBArF) as a chloride ion abstractor. The results of ethylene oligomerization with complexes **Pd1−Pd5** are summarized in Table 2. All the Pd(II) complexes exhibited moderate catalytic activities and yielded colorless oils with low densities under experimental conditions. Notably, the branching density and catalytic activity of the obtained ethylene oligomers increased with increasing temperature, whereas the MW tended to decline. These findings demonstrate that the elevated temperatures

favor chain transfer and chain walking reactions over chain propagation, while they also increase the rates of ethylene insertion (Figure 4). The experiments of the influence of the remote conjugated electronic effects (H, Me, tBu, F, and Cl) on ethylene oligomerization revealed that the catalysts **Pd3−Pd4** with electron-withdrawing substituents (F and Cl) yielded low-MW ethylene oligomers with high catalytic activities (Figure 4a,b), which were in good agreement with previous findings.[22,23] The complex **Pd5** with an electron-donating and bulky tBu group yielded the highest MW and branching density of ethylene oligomers at ambient temperature (Table 2, entry 9).

Our recent studies reported that the iminopyridyl Pd(II) catalysts could be effective for the copolymerization of olefins (ethylene or propylene) and polar monomers, leading to the generation of a series of polar functionalized polyolefin components with high incorporation ratios and tunable MWs.[26−29] In this study, polar functionalized ethylene/MA co-oligomers with low MWs and varying incorporation ratios were generated via the ethylene/MA co-oligomerization using complexes **Pd1−Pd5** (Table 3). The Pd(II) complexes exhibited moderate (10$^4$ g mol$^{-1}$ h$^{-1}$) co-oligomerization activities, which were lower than their homo-oligomerization activities, probably due to the inhibitory effect of the polar functional substituents (Table 3 vs 2). Similar to ethylene homo-oligomerization, the catalysts **Pd3−Pd4** with electron-withdrawing substituents (F and Cl) resulted in lower MW ethylene/MA co-oligomers with higher catalytic activities and lower incorporation ratios than the catalysts **Pd1−Pd2** and **Pd5**. Furthermore, the catalyst **Pd5** with the electron-donating and bulky tBu group yielded the highest MW ethylene/MA co-oligomers with the highest incorporation ratio (402, 4.92 mol % at 0.5 M MA; Table 3, entry 5) compared with other catalysts **Pd1−Pd4**. With increase in the MA concentration, the co-oligomerization activities decreased, while the incorporation ratios and MWs were significantly enhanced. For the ethylene/MA co-oligomers from Table 3, entry 7, more than one polar functionalized group per chain on average were obtained.

## 2.4. Microstructure Analysis of the Obtained Oligomers and Co-oligomers

The $^{13}$C NMR analysis indicated the branching patterns of ethylene oligomers and ethylene/MA co-oligomers (Table 4 and Figures 5 and 6). All oligomers and co-oligomers contained hyperbranched structures, as evidenced by the existence of sec-butyl groups.[49,50] For example, in the $^{13}$C NMR spectrum of the ethylene oligomer in entry 5, Table 2, resonances at 11.50 and 19.42 ppm confirm the formation of sec-butyl branches (Figure 5a,b). The oligomerization temper-
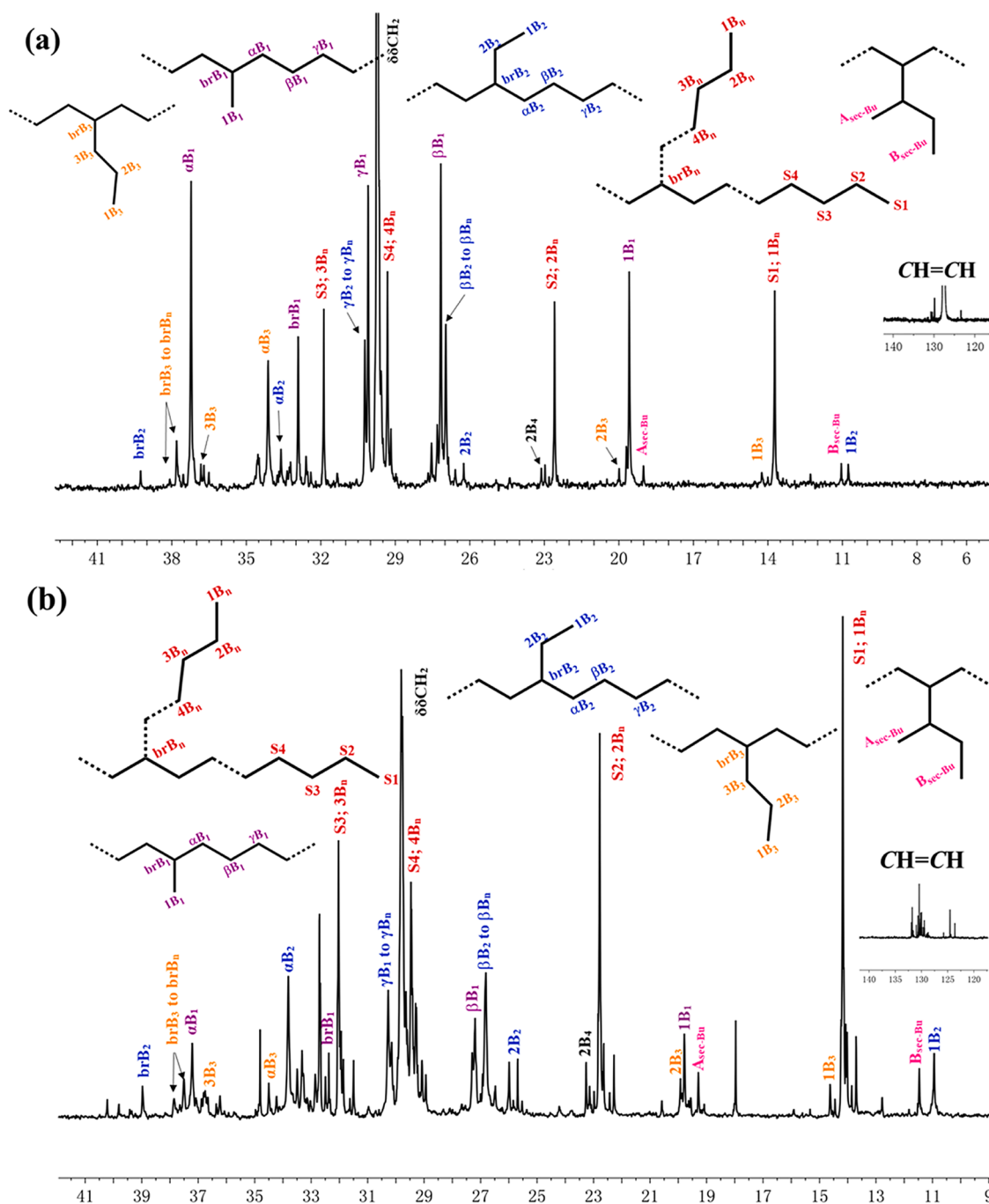
**Figure 5.** Detailed analysis of the $^{13}$C NMR spectrum of hyperbranched ethylene oligomers obtained by using **Ni3** at 70 °C (Table 1, entry 9, a) and using **Pd3** at 30 °C (Table 2, entry 5, b). Assignments are numbered according to refs 51−53. Chain ends are assigned with S1−S4. Branches are labeled as xBy, where y is the branch length and x is the carbon, starting from the methyl end with 1. The methine groups for the different branch lengths are labeled as brBy. A and B are the methyl groups of a *sec*-butyl branch.

ature not only affects the total branching of ethylene oligomers but also affects the branching distribution. A higher oligomerization temperature enhances the proportion of long-chain branching of ethylene oligomers, especially the branch-on-branch moiety (Table 4, entries 1−5), which suggests that hyperbranching in this system can be tuned by temperature. Particularly, the ethylene oligomers obtained from Ni(II) complexes mainly comprised methyl branches (50−55%) and significant amounts (38−40%) of long-chain branches, while those obtained by Pd(II) complexes had less bulkier compositions of methyl branches (13−16%) and

significantly higher amounts of long-chain branches (70−71%). This shows that the Pd(II) species can carry out more in-depth chain isomerization and give a more topological molecular structure than the corresponding nickel species. The $^{13}$C NMR spectrum of the ethylene−MA co-oligomer from entry 3, Table 3, reveals the presence of methyl, ethyl, *n*-propyl, and long-chain branches, an internal double bond, an obvious ester carbonyl group, and a branch-on-branch moiety (Figure 6). The observed findings indicate that the ethylene−MA co-oligomer is hyperbranched, and the COOMe units are predominantly incorporated at the end of the co-oligomer
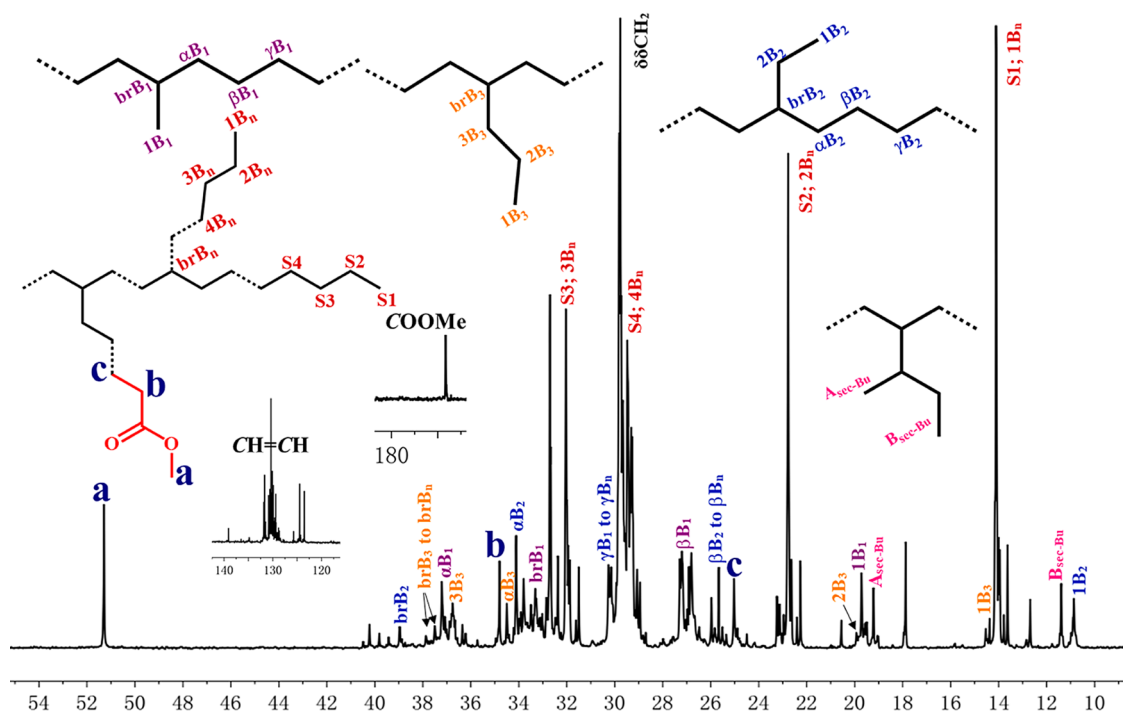
**Figure 6.** Detailed analysis of the $^{13}C$ NMR spectrum of a hyperbranched ethylene−MA co-oligomer obtained by using **Pd3** at 0.5 M MA from Table 3, entry 3. Assignments are numbered according to refs 22, 23 and 51−53. Chain ends are assigned with S1−S4. Branches are labeled as xBy, where y is the branch length and x is the carbon, starting from the methyl end with 1. The methine groups for the different branch lengths are labeled as brBy. A and B are the methyl groups of a *sec*-butyl branch.

branches. The differential scanning calorimetry analysis revealed that all low-MW hyperbranched oligomers and ethylene/MA co-oligomers appeared as viscous fluids and did not exhibit any phase transitions (melting or crystallization).

## 3. CONCLUSIONS

In summary, a series of *N*-terphenyl iminopyridyl ligands and the corresponding Pd(II) and Ni(II) complexes bearing remote conjugated substituents with different electronic effects (H, Me, *t*Bu, F, and Cl) were synthesized and characterized. The Pd(II) and Ni(II) complexes were used for ethylene oligomerization and co-oligomerization with MA. In the ethylene oligomerization catalyzed by Ni(II) complexes, **Ni1−Ni5** showed extremely high catalytic activities (5.52−7.74 × 10⁶ g·mol⁻¹·h⁻¹) and generated highly branched (54−71/1000 C) ethylene oligomers with low MWs (ca. 1−2 kg/mol). In the ethylene oligomerization catalyzed by Pd(II) complexes, **Pd1−Pd5** exhibited moderate catalytic activities (ca. 10⁴ g mol⁻¹ h⁻¹) and yielded highly branched (66−103/1000 C) ethylene oligomers with low MWs (260−787 g/mol). The Pd(II) catalysts with electron-withdrawing substituents (F and Cl) generated lower MW ethylene oligomers with higher activities when compared to those with electron-donating substituents. For ethylene−MA co-oligomerization, similar results were obtained with regard to the branching density, catalytic activity, and MW. In addition, the ethylene oligomers and ethylene−MA co-oligomers produced by *N*-terphenyl iminopyridyl Pd(II) and Ni(II) complexes contained hyperbranched structures. Notably, the ethylene oligomers obtained using Ni(II) complexes mainly comprised methyl branches and considerable amounts of long-chain branches, while those obtained using Pd(II) complexes had less bulkier compositions

of methyl branches and significantly higher amounts of long-chain branches (up to 83%). These results indicate that the *N*-terphenyl iminopyridyl catalysts are very conducive to the preparation of hyperbranched ethylene oligomers and co-oligomers with various microstructures. The remote conjugated electron effect showed little effect on the polymerization parameters of the iminopyridyl system, which is very different from the salicylaldiminato Ni(II) system.

## ■ ASSOCIATED CONTENT

### ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acspolymersau.1c00039.

> Full experimental details for the synthetic procedures, materials, analytical methods, NMR and mass spectra of synthetic compounds, and NMR and GPC curves of oligomer and co-oligomer samples (PDF)

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## Author Contributions

‖H.F. and G.C. are equal first authors.

## Notes

The authors declare no competing financial interest.
CCDC numbers of complexes **Ni3** and **Pd4** are 2109732−2109733. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## ■ REFERENCES

(1) Wiedemann, T.; Voit, G.; Tchernook, A.; Roesle, P.; Göttker-Schnetmann, I.; Mecking, S. Monofunctional Hyperbranched Ethylene Oligomers. *J. Am. Chem. Soc.* **2014**, *136*, 2078−2085.

(2) Mecking, S.; Schnitte, M. Neutral Nickel(II) Catalysts: From Hyperbranched Oligomers to Nanocrystal-Based Materials. *Acc. Chem. Res.* **2020**, *53*, 2738−2752.

(3) Stephenson, C. J.; McInnis, J. P.; Chen, C.; Weberski, M. P.; Motta, A.; Delferro, M.; Marks, T. J. Ni(II) Phenoxyiminato Olefin Polymerization Catalysis: Striking Coordinative Modulation of Hyperbranched Polymer Microstructure and Stability by a Proximate Sulfonyl Group. *ACS Catal.* **2014**, *4*, 999−1003.

(4) Falivene, L.; Wiedemann, T.; Göttker-Schnetmann, I.; Caporaso, L.; Cavallo, L.; Mecking, S. Control of Chain Walking by Weak Neighboring Group Interactions in Unsymmetrical Catalysts. *J. Am. Chem. Soc.* **2018**, *140*, 1305−1312.

(5) Xiang, P.; Ye, Z. Synthesis and characterization of low- and medium-molecular-weight hyperbranched polyethylenes by chain walking ethylene polymerization with Pd-diimine catalysts. *Polymer* **2011**, *52*, 5027−5039.

(6) Meduri, A.; Montini, T.; Ragaini, F.; Fornasiero, P.; Zangrando, E.; Milani, B. Palladium-Catalyzed Ethylene/Methyl Acrylate Cool-igomerization: Effect of a New Nonsymmetric α-Diimine. *ChemCatChem* **2013**, *5*, 1170−1183.

(7) Guo, L.; Liu, W.; Li, K.; Sun, M.; Sun, W.; Zhao, L.; Jiang, G.; Peng, H.; Liu, Z.; Dai, S. Synthesis of functional and hyperbranched ethylene oligomers using unsymmetrical α-diimine palladium catalysts. *Eur. Polym. J.* **2019**, *115*, 185−192.

(8) Cruz, T. F. C.; Cruz, C. F.; Luís, F. V.; Gomes, P. T. Benzylnickel(II) Complexes of 2-Iminopyrrolyl Chelating Ligands: Synthesis, Structure, and Catalytic Oligo-/Polymerization of Ethylene to Hyperbranched Polyethylene. *Organometallics* **2021**, *40*, 2594−2609.

(9) Bianchini, C.; Giambastiani, G.; Luconi, L.; Meli, A. Olefin oligomerization, homopolymerization and copolymerization by late transition metals supported by (imino)pyridine ligands. *Coord. Chem. Rev.* **2010**, *254*, 431−455.

(10) Laine, T. V.; Lappalainen, K.; Liimatta, J.; Aitola, E.; Löfgren, B.; Leskelä, M. Polymerization of ethylene with new diimine complexes of late transition metals. *Macromol. Rapid Commun.* **1999**, *20*, 487−491.

(11) Laine, T. V.; Piironen, U.; Lappalainen, K.; Klinga, M.; Aitola, E.; Leskelä, M. Pyridinylimine-based nickel(II) and palladium(II) complexes: preparation, structural characterization and use as alkene polymerization catalysts. *J. Organomet. Chem.* **2000**, *606*, 112−124.

(12) Meneghetti, S. P.; Lutz, P. J.; Kress, J. Oligomerization of olefins catalyzed by new cationic palladium(II) complexes containing an unsymmetrical α-diimine ligand. *Organometallics* **1999**, *18*, 2734−2737.

(13) Huang, C.; Zhang, Y.; Liang, T.; Zhao, Z.; Hu, X.; Sun, W.-H. Rigid geometry 8-arylimino-7, 7-dimethyl-5, 6-dihydroquinolyl nickel bromides: single-site active species towards ethylene polymerization. *New J. Chem.* **2016**, *40*, 9329−9336.

(14) Sun, Z.; Huang, F.; Qu, M.; Yue, E.; Oleynik, I. V.; Oleynik, I. I.; Zeng, Y.; Liang, T.; Li, K.; Zhang, W.; Sun, W.-H. Targeting polyethylene waxes: 9-(2-cycloalkylphenylimino)-5, 6, 7, 8-tetrahy-drocycloheptapyridylnickel halides and their use as catalysts for ethylene polymerization. *RSC Adv.* **2015**, *5*, 77913−77921.

(15) Huang, F.; Sun, Z.; Du, S.; Yue, E.; Ba, J.; Hu, X.; Liang, T.; Galland, G. B.; Sun, W.-H. Ring-tension adjusted ethylene polymerization by ariliminocycloheptapyridyl nickel complexes. *Dalton Trans.* **2015**, *44*, 14281−14292.

(16) Sun, Z.; Yue, E.; Qu, M.; Oleynik, I. V.; Oleynik, I. I.; Li, K.; Liang, T.; Zhang, W.; Sun, W.-H. 8-(2-Cycloalkylphenylimino)-5, 6, 7-trihydro-quinolylnickel halides: polymerizing ethylene to highly branched and lower molecular weight polyethylenes. *Inorg. Chem. Front.* **2015**, *2*, 223−227.

(17) Yue, E.; Xing, Q.; Zhang, L.; Shi, Q.; Cao, X.-P.; Wang, L.; Redshaw, C.; Sun, W.-H. Synthesis and characterization of 2-(2-benzhydrylnaphthyliminomethyl) pyridylnickel halides: formation of branched polyethylene. *Dalton Trans.* **2014**, *43*, 3339−3346.

(18) Sun, W.-H.; Song, S.; Li, B.; Redshaw, C.; Hao, X.; Li, Y.-S.; Wang, F. Ethylene polymerization by 2-iminopyridylnickel halide complexes: synthesis, characterization and catalytic influence of the benzhydryl group. *Dalton Trans.* **2012**, *41*, 11999−12010.

(19) Wang, C.; Zhang, Y.; Mu, H.; Jian, Z. Systematic studies on dibenzhydryl and pentiptycenyl substituted pyridine-imine nickel(II) mediated ethylene polymerization. *Dalton Trans.* **2020**, *49*, 4824−4833.

(20) Guo, L.; Li, S.; Ji, M.; Sun, W.; Liu, W.; Li, G.; Zhang, J.; Liu, Z.; Dai, S. Monoligated vs Bisligated Effect in Iminopyridyl Nickel Catalyzed Ethylene Polymerization. *Organometallics* **2019**, *38*, 2800−2806.

(21) Chen, X.-L.; Gao, J.; Liao, H.; Gao, H.-Y.; Wu, Q. Synthesis, characterization, and catalytic ethylene oligomerization of pyridine-imine palladium complexes. *Chin. J. Polym. Sci.* **2018**, *36*, 176−184.

(22) Li, S.; Lu, Z.; Fan, W.; Dai, S. Efficient incorporation of a polar comonomer for direct synthesis of hyperbranched polar functional ethylene oligomers. *New J. Chem.* **2021**, *45*, 4024−4031.

(23) Yan, Z.; Li, S.; Dai, S. Synthesis and Characterization of Hyperbranched Polar Functionalized Olefin Oligomers. *Chin. J. Synth. Chem.* **2021**, 1005-51.

(24) Chen, Z.; Allen, K. E.; White, P. S.; Daugulis, O.; Brookhart, M. Synthesis of branched polyethylene with "half-sandwich" pyridine-imine nickel complexes. *Organometallics* **2016**, *35*, 1756−1760.

(25) Dai, S.; Sui, X.; Chen, C. Synthesis of high molecular weight polyethylene using iminopyridyl nickel catalysts. *Chem. Commun.* **2016**, *52*, 9113−9116.

(26) Dai, S.; Li, S. Effect of aryl orientation on olefin polymerization in iminopyridyl catalytic system. *Polymer* **2020**, *200*, 122607.

(27) Peng, H.; Li, S.; Li, G.; Dai, S.; Ji, M.; Liu, Z.; Guo, L. Rotation-restricted strategy to synthesize high molecular weight polyethylene using iminopyridyl nickel and palladium catalyst. *Appl. Organomet. Chem.* **2021**, *35*, No. e6140.

(28) Ge, Y.; Li, S.; Wang, H.; Dai, S. Synthesis of Branched Polyethylene and Ethylene-MA Copolymers Using Unsymmetrical Iminopyridyl Nickel and Palladium Complexes. *Organometallics* **2021**, *40*, 3033−3041.

(29) Li, S.; Dai, S. Highly efficient incorporation of polar comonomers in copolymerizations with ethylene using iminopyridyl palladium system. *J. Catal.* **2021**, *393*, 51−59.

(30) Saki, Z.; D'Auria, I.; Dall'Anese, A.; Milani, B.; Pellecchia, C. Copolymerization of Ethylene and Methyl Acrylate by Pyridylimino Ni(II) Catalysts Affording Hyperbranched Poly(ethylene-co-methyl acrylate)s with Tunable Structures of the Ester Groups. *Macromolecules* **2020**, *53*, 9294−9305.

(31) D'Auria, I.; Milione, S.; Caruso, T.; Balducci, G.; Pellecchia, C. Synthesis of hyperbranched low molecular weight polyethylene oils by an iminopyridine nickel(II) Catalyst. *Polym. Chem.* **2017**, *8*, 6443−6454.

(32) Rosa, V.; Avilés, T.; Aullon, G.; Covelo, B.; Lodeiro, C. A new bis (1-naphthylimino) acenaphthene compound and its Pd(II) and Zn(II) complexes: synthesis, characterization, solid-state structures and density functional theory studies on the syn and anti isomers. *Inorg. Chem.* **2008**, *47*, 7734−7744.

(33) Guo, L.; Kong, W.; Xu, Y.; Yang, Y.; Ma, R.; Cong, L.; Dai, S.; Liu, Z. Large-scale synthesis of novel sterically hindered acenaphthene-based α-diimine ligands and their application in coordination chemistry. *J. Organomet. Chem.* **2018**, *859*, 58−67.

(34) Li, S.; Dai, S. 8-Arylnaphthyl substituent retarding chain transfer in insertion polymerization with unsymmetrical α-diimine systems. *Polym. Chem.* **2020**, *11*, 7199−7206.

(35) Dai, S.; Li, S.; Xu, G.; Wu, C.; Liao, Y.; Guo, L. Flexible Cycloalkyl Substituents in Insertion Polymerization with α-Diimine Nickel and Palladium Species. *Polym. Chem.* **2020**, *11*, 1393−1400.

(36) Guo, L.; Sun, W.; Li, S.; Xu, G.; Dai, S. Bulky yet flexible substituents in insertion polymerization with α-diimine nickel and palladium systems. *Polym. Chem.* **2019**, *10*, 4866−4871.

(37) Gates, D. P.; Svejda, S. A.; Oñate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. Synthesis of branched polyethylene using (α-diimine) nickel(II) catalysts: influence of temperature, ethylene pressure, and ligand structure on polymer properties. *Macromolecules* **2000**, *33*, 2320−2334.

(38) Dai, S.; Li, G.; Lu, W.; Liao, Y.; Fan, W. Suppression of Chain Transfer via Restricted Rotation Effect of Dibenzosuberyl Substituents in Polymerization Catalysis. *Polym. Chem.* **2021**, *12*, 3240−3249.

(39) Gong, Y.; Li, S.; Gong, Q.; Zhang, S.; Liu, B.; Dai, S. Systematic investigations of ligand steric effects on α-diimine nickel catalyzed olefin polymerization and copolymerization. *Organometallics* **2019**, *38*, 2919−2926.

(40) Ge, Y.; Li, S.; Fan, W.; Dai, S. Flexible "Sandwich" (8-Alkylnaphthyl α-Diimine) Catalysts in Insertion Polymerization. *Inorg. Chem.* **2021**, *60*, 5673−5681.

(41) Gong, Y.; Li, S.; Tan, C.; Kong, W.; Xu, G.; Zhang, S.; Liu, B.; Dai, S. π−π interaction effect in insertion polymerization with α-diimine palladium systems. *J. Catal.* **2019**, *378*, 184−191.

(42) Zuideveld, M. A.; Wehrmann, P.; Röhr, C.; Mecking, S. Remote Substituents Controlling Catalytic Polymerization by very Active and Robust Neutral Nickel(II) Complexes. *Angew. Chem., Int. Ed.* **2004**, *43*, 869−873.

(43) Weberski, M. P.; Chen, C.; Delferro, M.; Zuccaccia, C.; Macchioni, A.; Marks, T. J. Suppression of β-Hydride Chain Transfer in Nickel(II)-Catalyzed Ethylene Polymerization via Weak Fluoro-carbon Ligand-Product Interactions. *Organometallics* **2012**, *31*, 3773−3789.

(44) Osichow, A.; Göttker-Schnetmann, I.; Mecking, S. Role of Electron-Withdrawing Remote Substituents in Neutral Nickel(II) Polymerization Catalysts. *Organometallics* **2013**, *32*, 5239−5242.

(45) Li, S.; Xu, G.; Dai, S. A remote nonconjugated electron effect in insertion polymerization with α-diimine nickel and palladium species. *Polym. Chem.* **2020**, *11*, 2692−2699.

(46) Hu, X.; Kang, X.; Zhang, Y.; Jian, Z. Facile Access to Polar-Functionalized Ultrahigh Molecular Weight Polyethylene at Ambient Conditions. *CCS Chem.* **2021**, *3*, 1598−1612.

(47) Hu, X.; Zhang, Y.; Li, B.; Jian, Z. Horizontally and Vertically Concerted Steric Strategy in α-Diimine Nickel Promoted Ethylene (Co)Polymerization. *Chin. J. Chem.* **2021**, *39*, 2829−2836.

(48) Hu, X.; Zhang, Y.; Li, B.; Jian, Z. Fluorinated α-Diimine Nickel Mediated Ethylene (Co)Polymerization. *Chem.—Eur. J.* **2021**, *27*, 11935−11942.

(49) Voit, B. I.; Lederer, A. Hyperbranched and Highly Branched Polymer Architectures-Synthetic Strategies and Major Characterization Aspects. *Chem. Rev.* **2009**, *109*, 5924−5973.

(50) Dong, Z.; Ye, Z. Hyperbranched polyethylenes by chain walking polymerization: synthesis, properties, functionalization, and applications. *Polym. Chem.* **2012**, *3*, 286−301.

(51) Cotts, P. M.; Guan, Z.; McCord, E.; McLain, S. Novel Branching Topology in Polyethylenes As Revealed by Light Scattering and $^{13}$C NMR. *Macromolecules* **2000**, *33*, 6945−6952.

(52) Randall, J. C. A review of high-resolution liquid carbon-13 nuclear magnetic resonance characterizations of ethylene-based polymer. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1989**, *29*, 201−317.

(53) Galland, G. B.; De Souza, R. F.; Mauler, R. S.; Nunes, F. F. $^{13}$C NMR Determination of the Composition of Linear Low-Density Polyethylene Obtained with [$\eta^3$-Methallyl-nickel-diimine]PF$_6$ Complex. *Macromolecules* **1999**, *32*, 1620−1625.