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Rotation-restricted strategy to synthesize high molecular weight polyethylene using iminopyridyl nickel and palladium catalyst

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Most of the iminopyridyl Ni (II) and Pd (II) catalysts are reported to oligomerize ethylene or yield very low molecular weight polyethylene. Moreover, the molecular weight of product is not sensitive to ligand sterics. In this contribution, we demonstrate that the bulky rotation-restricted substituents incorporated into iminopyridyl Ni (II) and Pd (II) catalysts that provide the right orientation are highly effective in retarding the chain transfer. Thus, (2,6-bis(10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl)-4-methylphenyl)-1-(pyridin-2-yl)methanimine nickel (II) bromide (**Ni3**) and (2,6-bis(10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-yl)-4-methylphenyl)-1-(pyridin-2-yl) methanimine palladium (II) methyl chloride (**Pd3**) with the phenyl substituents fixed in the diarylmethyl moiety produce polyethylene or functionalized polyethylene (ethylene-MA copolymer) with high M_n values up to 2.5×10^4 g mol^{-1}, while allowing the high MA incorporation (3.2%–13.8%). In addition, the effects on the (co)polymerization behavior as a function of rotation-restricted substituent variations (free rotation, restricted rotation and fixation) were systemically studied. As a result, various molecular weight polyethylene and ethylene-MA copolymer with high MA incorporation ratio were also obtained in this system.

KEYWORDS

ethylene copolymerization, ethylene polymerization, iminopyridyl, Nickel, Palladium

1 | INTRODUCTION

Late transition metal catalysts for olefin coordination-insertion polymerization have received great attention since the seminal discovery of Ni (II) and Pd (II)

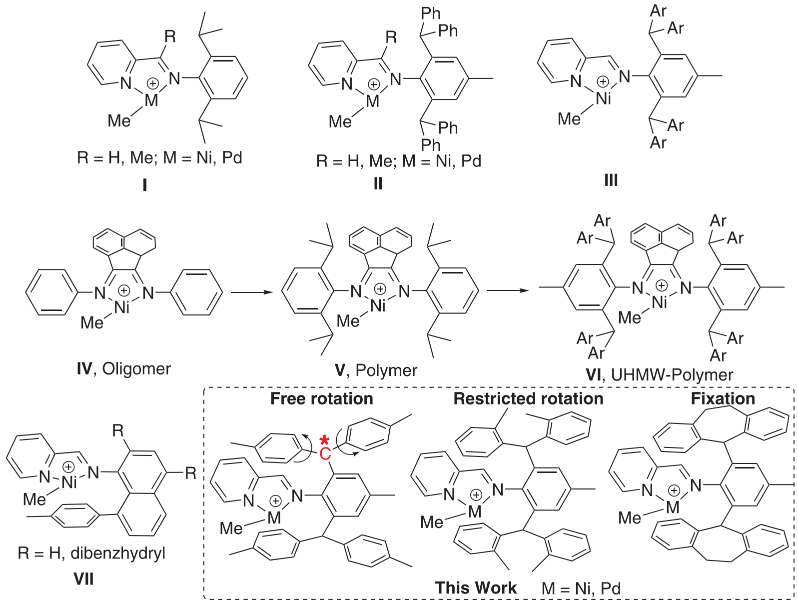
The first two authors are equal first authors.

[Correction added on 19 January 2021, after first online publication: The note identifying the first authors had been mistakenly omitted.]

α-diimine catalysts.[1] The key to convert olefins to high molecular weight polymers for these catalysts is the incorporation of sterically bulky axial substituents on the ligand since bulk can inhibit the chain transfer process. Particularly, in contrast to early transition metal catalysts, late transition metal catalysts not only could produce branched polyolefins by extensive chain walking process but also generate the functional polyolefins by the copolymerization of olefins with polar monomers due to their low oxophilicity.[2–7]

In addition to the α-diimine catalysts, some interesting results also have been revealed for [N, N] bidentate iminopyridyl Ni (II) and Pd (II) catalysts.[8–10] For example, Laine discovered that the dimeric iminopyridyl Ni (II) catalysts generated low molecular weight polyethylene (Scheme 1, **I**, M_n < 3,500 at temperature above 20°C).[11,12] By using bulkier dibenzhydryl group, more active Ni (II) catalysts are obtained. However, the molecular weight of polyethene in this system is still very low (Scheme 1, **II**, M_n < 1,000).[13] Gao and coworkers also reported that iminopyridyl Pd (II) catalysts with the same dibenzhydryl group produced highly branched oils (Scheme 1, **II**, M_n: 600–800).[14] Recently, our group investigated the mono-ligated and bis-ligated effect of the iminopyridyl Ni (II) catalysts with very bulky diarylmethyl moieties on the catalytic activity and the structure (e.g., molecular weight and branching density) of polyethylene. Similarly, the low molecular weight polyethylene is produced (Scheme 1, **III**, M_n < 8,300 at temperature above 20°C).[15] Basically, these catalysts showed high activity for ethylene polymerization while produced oligomers or low-molecular-weight polyethylene since only a single *ortho*-disubstituted aryl imine structure is sterically incorporated compared to the symmetric α-diimine system.

Some strategies, including steric tuning of *ortho* substituents on the N-aryl ring,[16–23] the introduction of bulky substituents on the backbone[24–27] and electronic perturbation,[28–30] have been used to increase the molecular weight of polyolefins in the α-diimine catalysts system. Among them, the modification of sterically bulky *ortho*-aryl substituents is the most effective approach to access high molecular weight polyolefins. For example, α-diimine Ni (II) catalysts with *ortho*-H substituents on both aryl rings oligomerize ethylene due to the incidental β-H elimination (Scheme 1, **IV**).[2] When the bulky substituent 2,6-diisopropyl is employed, high molecular weight polyolefins can be produced (Scheme 1, **V**).[1] Further, using the bulkier dibenzhydryl or diarylmethyl instead of diisopropyl, ultrahigh molecular weight polyethylene (UHMWPE) is obtained (Scheme 1, **VI**).[26,31] α-diimine Pd (II) catalysts also showed the similar trend that the increase in steric bulk of *ortho*-aryl substituents improved the molecular weight of the polyolefin.[32–34] Thus, the strategy to introduce substituents with bulky steric hindrance in the α-diimine ligands has been extremely studied in this field. However, as mentioned above, this strategy most often showed no improvement for iminopyridyl Ni (II) and Pd (II) catalysts. One exception example was the "half-sandwich" iminopyridyl Ni (II) catalysts bearing the naphthyl moieties (Scheme 1, **VII**).[35,36] These catalysts provided effective axial shielding and retarded chain transfer, thus affording polyethylene with high molecular weight. This story told us that the orientation of bulky substituent is very important in iminopyridyl Ni (II) and Pd (II) system. On the



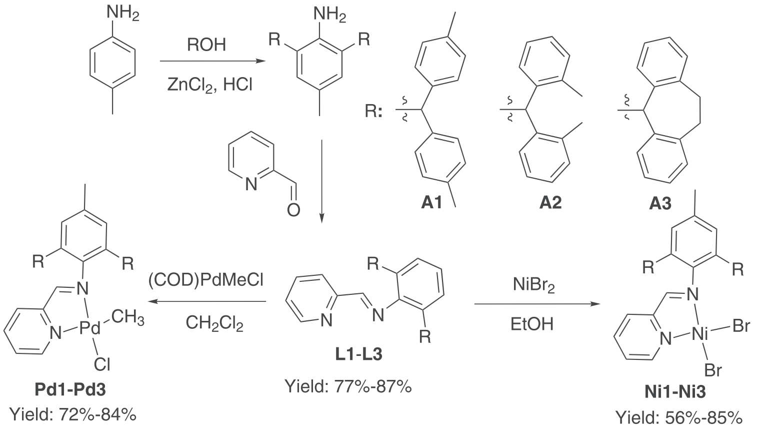
SCHEME 1 The reported iminopyridyl Ni (II) and Pd (II) catalysts (**I–III**, **VII**), steric tuning of *ortho* substituents for α-diimine catalysts system (**IV–VI**) and our current work

other hand, Guan and coworkers showed that their cyclophane-based α-diimine Ni (II) and Pd (II) catalysts could produce higher molecular weight polyethylene and incorporate more methyl acrylate (MA) in ethylene-MA copolymerization than the acyclic analogs.[29,37,38] Gao and coworkers also displayed that increasing the steric hindrance of the backbone structure for α-diimine catalysts can decrease the associate chain transfer.[24,39–43] The cyclophane design and the bulky backbone hinder rotation of the catalyst's axial steric environment in these α-diimine systems. In the system of iminopyridyl catalysts with the dibenzhydryl group, the two phenyl substituents in the dibenzhydryl moiety rotate freely around the central C atom (Scheme 1, **C***), which can influence the orientation and the effective steric hindrance of this bulky substituent. If this rotation is restricted, it is possible to retard chain transfer sufficiently and result in the production of high molecular weight polyolefins. On the basis of these considerations, we report here the rotation-restricted strategy to increase the molecular weight of polyolefins in iminopyridyl Ni (II) and Pd (II) systems. In particular, the degree of restricted rotation (free rotation, restricted rotation and fixation) on the catalytic properties toward ethylene polymerization and copolymerization with MA was systemically studied. Most surprisingly, the high molecular weight ethylene-MA copolymer with high MA incorporation ratio was also obtained using the iminopyridyl Pd (II) catalysts in this system.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis and characterization of the complexes

The anilines **A1–A3** were synthesized by the dialkylation of *p*-toluidine with the substituted benzhydrol in the presence of hydrochloric acid and zinc chloride (Schemes S1 and S2 and Figures S4–S7). The iminopyridine ligands **L1–L3** were subsequently produced by the acid-catalyzed condensation reaction of **A1–A3** with picolinaldehyde (Scheme 2, Figures S8–S11, S18, and S19). Compared to the reported the “half-sandwich” iminopyridyl ligands bearing the naphthyl moieties,[35,36] these ligands can be more easily large-scale synthesized through simple reactions by the reagents commercially available with no chromatography involved. Treatment of the ligands with $NiBr_2$ in ethanol afforded the corresponding mono-ligated Ni (II) complexes **Ni1–Ni3**. **Ni1** already described in our recent work[15] was used for comparison with this series of complexes. Identity and purity of **Ni2** and **Ni3** were established by mass spectrometry (Figures S20 and S21) and elemental analysis. Notably, we recently reported that the reaction of **L1** with $(DME)NiBr_2$ (DME = ethylene glycol dimethyl ether) in CH_2Cl_2 solution led to the bis-ligated Ni (II) complex (nickel center is surrounded by two bidentate ligands). The production of mono-ligated complex **Ni1** and the corresponding bis-ligated complex with the same ligand depended on the selection of solvents and metal precursors.[15] Herein, **L2** and **L3**, which showed the higher steric hindrance than **L1** (*ortho*-substituted, *ortho*-bridged vs. *para*-substituted), were also employed to react with $(DME)NiBr_2$ in CH_2Cl_2 solution. However, according to the results of elemental analysis and mass spectrometry, the obtained products were still the mono-ligated Ni (II) complexes. This result indicated that the introduction of *ortho*-substituent and *ortho*-bridged substituent significantly increased the steric hindrance of the ligands and made it difficult to form the bis-ligated complexes. Likewise, the palladium complexes **Pd1–Pd3** were also readily formed from the reaction of the ligands **L1–L3** with (COD)PdMeCl (COD = 1,5-cycloocta diene) and fully identified by NMR (Figures S12–S17), mass spectrometry (Figures S22–S24),



SCHEME 2 Synthesis of iminopyridine ligands and the corresponding iminopyridyl Ni (II) and Pd (II) complexes

and elemental analysis. All of these palladium complexes showed the mono-ligated coordination mode, which are similar with the previously reported iminopyridyl Pd (II) complexes containing dibenzhydryl moiety (Scheme 1, **II**).[14]

Single crystals of **Ni3** and **Pd3** were obtained by layering their CH_2Cl_2 solution with hexane at ambient temperature (Figure 1 and Table S1). In contrast to the mono-ligated complex **Ni1** with *para*-methyl substituents, which crystallized as a centrosymmetric dimer (bridged-bromide) and adopted a distorted octahedral geometry,[15] **Ni3** with more bulky *ortho*-bridged substituents showed the mononuclear structure with a distorted tetrahedral geometry at the nickel center. The phenyl substituents fixed in the diarylmethyl moiety for **Ni3** lie nearly parallel to the five-member chelate ring (Ni1-N1-C5-C6-N2) with both of the dihedral angles being 14.78°. Meanwhile, the dihedral angles between the phenyl rings in the diarylmethyl moiety and the five-member chelate ring for our reported **Ni1** (CCDC number: 1816867) are 48.75° (below) and 16.85° (above), respectively,[15] and much larger than those of **Ni3**. Thus, the fixation of the phenyl substituents in **Ni3** provided effective blockage and shielding of the axial positions of the metal center and would be able to retard the associative chain transfer process. The palladium center for **Pd3** showed a distorted square-planar geometry. Similarly, the phenyl rings in the diarylmethyl moiety are also nearly parallel to the five-member chelate ring (Pd1-N2-C2-C3-N1) for **Pd3** with the dihedral angles being 14.36° (below) and 11.49° (above), respectively. Further, the chemical shift of Pd-CH_3 for **Pd1** and **Pd2** is at δ 1.26 and 1.64 ppm in the ^{13}C NMR, respectively, while the corresponding peaks for **Pd3** are δ 0.38 ppm in the ^{13}C NMR. Such a big change in the chemical shift also can be attributed to the unique aryl orientation in **Pd3**.

2.2 | Ni (II)-catalyzed ethylene polymerization

Upon activation with $AlEt_2Cl$, all of the Ni (II) complexes proved to be very high active toward ethylene polymerization (up to 1.1×10^7 g mol^{-1} h^{-1}, Table 1, entry 1). The polymerization results at the same temperature revealed the following trend in their activities: **Ni1** > **Ni3** > **Ni2**. The observed decreasing activity trend can be accounted for by the increasing bulkiness of the substituents, going from *para*-CH_3 to *ortho*-CH_3 or *ortho*-bridged CH_2. In accord with the previous report, a less bulky group allowed for a faster monomer trapping and consequently higher activity.[13] However, **Ni2** with *ortho*-CH_3 is less active than **Ni3** with *ortho*-bridged CH_2. Considering the similar steric hindrance of *ortho*-CH_3 and *ortho*-bridged CH_2, the orientation of these bulky substituents, apparently as a result of the degree of restricted rotation, also plays a key role in determining the catalyst activity. The striking feature of these results is increasing the degree of restricted rotation from *para*-CH_3 in **Ni1** (free rotation) to *ortho*-CH_3 in **Ni2** (restricted rotation), and *ortho*-bridged CH_2 in **Ni3** (fixation) led to a dramatic increase in molecular weight of the obtained polyethylene (Figures S50–S55). For example, M_n of the polyethylene

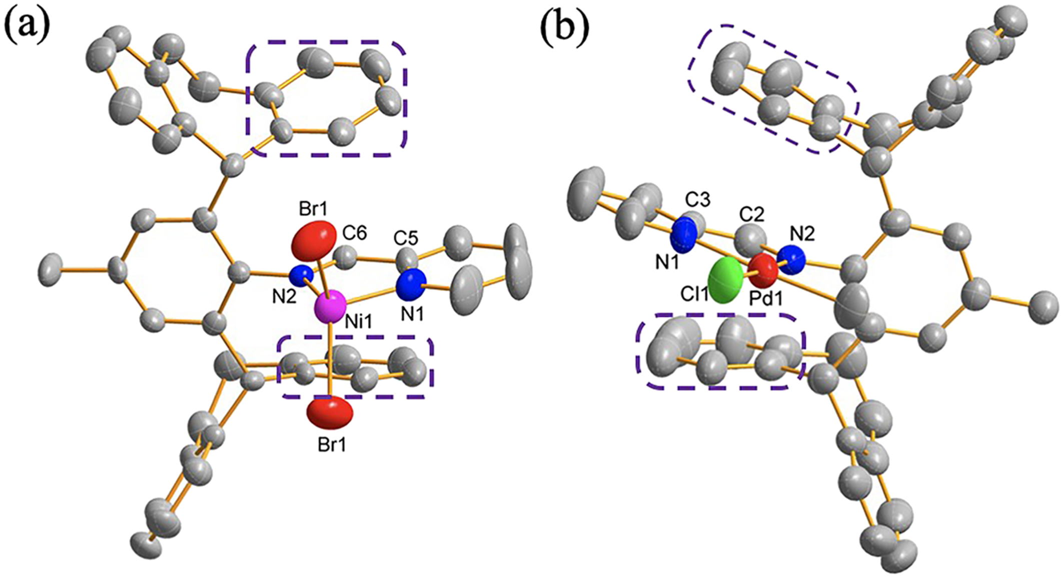


FIGURE 1 Solid-state molecular structures of nickel complex **Ni3** (a) and palladium complex **Pd3** (b) with 50% probability level, and H atoms have been omitted for clarity

TABLE 1 Ethylene polymerization with Ni (II) catalysts

Entry	Catalyst	T/°C	Yield/g	Act.[a]	M_n[b]	PDI[b]	B[c]	T_m[d]
1	**Ni1**	30	5.53	11.1	1,200	1.83	56	55
2	**Ni1**	50	5.39	10.8	1,000	1.90	57	Wax[e]
3	**Ni1**	70	2.33	4.7	900	1.71	58	Wax
4	**Ni2**	30	0.33	0.7	3,400	1.72	47	65
5	**Ni2**	50	0.82	1.6	2,000	2.30	48	58
6	**Ni2**	70	0.95	1.9	2,000	1.67	49	54
7	**Ni3**	30	2.89	5.8	24,300	2.07	52	74
8	**Ni3**	50	2.19	4.4	24,700	2.04	55	72
9	**Ni3**	70	1.43	2.9	7,500	3.09	66	63

Note: Conditions: Ni (II) catalyst (2 μmol), 200 eq. $AlEt_2Cl$, 1 ml of CH_2Cl_2, 29 ml toluene, 8 atm, polymerization time (15 min).

[a] Activity is in unit of 10^6 g mol^{-1} h^{-1}.

[b] M_n is in unit of g mol^{-1}, determined by GPC in trichlorobenzene at 150°C.

[c] B = branches per 1,000 carbons, determined by ^1H NMR spectroscopy, $B = 1{,}000 \times 2(I_{CH3})/3(I_{CH2+CH} + I_{CH3})$. Branching numbers for low molecular weight samples ($M_n < 10{,}000$) were corrected for end groups.

[d] Determined by differential scanning calorimetry (DSC), broad peak.

[e] Amorphous.

generated by **Ni3** are nearly 1 order of magnitude higher than that produced by **Ni1** and **Ni2** (M_n: 1,000–3,000 vs. 25,000 g mol^{-1}). Apparently, the molecular weight of the obtained polyethylene in iminopyridyl system is essentially governed by the orientation of the bulky substituents, which is determined by the degree of the restricted rotation and can provide effective axial shielding for the metal center. It should be noted that late transition metals such as nickel and palladium display a very high propensity for β-hydride elimination, which potentially leads to chain transfer in olefin polymerization.[4] The initial work by Brookhart showed that the key to obtain high molecular weight polymers using such catalysts is the incorporation of *ortho* substituents on the aryl imine groups which positions steric bulk at the two axial sites above and below the square coordination plane. Bulk at the two axial sites inhibits chain transfer relative to chain propagation, and thus, the high polymer molecular weight is achieved.[44] As aforementioned in single crystal analysis, *ortho*-bridged CH_2 in **Ni3** inhibits the rotation of two phenyl substituents in the dibenzhydryl moiety around the central C atom and enforces a more "vertical" orientation and axial shielding toward the metal center than *para*-CH_3 in **Ni1** and *ortho*-CH_3 in **Ni2**. In addition, the polyethylene generated by **Ni1** with less bulky *para*-CH_3 showed higher branching density than that by **Ni2** with *ortho*-CH_3 and **Ni3** with *ortho*-bridged CH_2 at 30°C and 50°C (Figures S25–S33). Accordingly, compared to the polyethylene generated by **Ni2** and **Ni3**, the polyethylene obtained by **Ni1** showed lower T_m or no T_m (wax) (Figures S44–S49). However, the polyethylene generated by **Ni3** showed the highest branching density at high temperature (70°C).

When the polymerization temperature increased from 30°C to 50°C and 70°C, the catalytic activity of **Ni1** and **Ni3** decreased and the branching density increased, which are consistent with previous observations.[35] However, the catalytic activity of **Ni2** increased by increasing the polymerization temperature. In addition, the molecular weight did not change significantly with increasing temperature for **Ni1**. In the case of **Ni2** and **Ni3**, the molecular weight dropped considerably as the polymerization temperature increased. However, the molecular weight of the polyethylene generated by **Ni3** at 70°C was still 7,500 g mol^{-1} and much higher than that obtained by **Ni1** and **Ni2**. This result indicated that the chain transfer was also effectively retarded at high temperature for **Ni3**.

2.3 | Pd (II)-catalyzed ethylene (co) polymerization

Upon the activation of excess sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBArF), ethylene polymerization and copolymerization with MA were carried out using these Pd (II) complexes. In ethylene polymerization, complexes **Pd1–Pd3** showed moderate activities under given conditions and generated highly branched ethylene oligomers (**Pd1** and **Pd2**) and polyethylene (**Pd3**) (Table 2). No clear trend was observed for the relationship between the catalytic activity and ligand

TABLE 2 Ethylene polymerization with Pd (II) catalysts

Entry	Cat.	*T* (°C)	yield (g)	Act.(10^4)[a]	M_n[b]	M_n[c]	M_w/M_n[c]	B[d]
1	**Pd1**	30	1.62	2.7	460	540	1.77	62
2	**Pd1**	50	7.70	12.8	270	310	1.37	83
3	**Pd2**	30	2.49	4.2	4,200	4,100	2.60	101
4	**Pd2**	50	4.26	7.1	2,500	2,300	1.42	105
5	**Pd3**	30	1.69	2.8	19,200	24,000	2.56	78
6	**Pd3**	50	6.96	11.6	15,600	13,400	2.78	85

Note: Reaction conditions: Pd (II) catalyst (20 μmol), NaBArF (1.5 equiv.), CH_2Cl_2 (40 mL), ethylene (4 atm), polymerization time (3 h).

[a] Activity is in unit of 10^4 g mol^{-1} h^{-1}.

[b] M_n is in unit of g mol^{-1}, determined by ^1H NMR spectroscopy.

[c] M_n is in unit of g mol^{-1}, determined by GPC in THF at 40°C versus polystyrene standards.

[d] B = branches per 1,000 carbons, determined by ^1H NMR spectroscopy, $B = 1{,}000 \times 2(I_{CH3})/3(I_{CH2+CH} + I_{CH3})$. Branching numbers for low molecular weight samples ($M_n < 10{,}000$) were corrected for end groups.

structure in Pd (II) system. In consistent with Ni (II) complexes, the restricted-rotation effect on the molecular weight of the obtained product was also significant for these Pd (II) complexes. The molecular weight of the obtained polyethylene by **Pd3** was approximately. 2 orders of magnitude higher than those by **Pd1** and 1 order of magnitude higher than those by **Pd2** (Table 2 and Figures S1, S2, and S56–S61), which further confirmed that the right orientation of aryl substituents is crucial for iminopyridyl Ni (II) and Pd (II) catalysts. Nevertheless, the polyethylene obtained by **Pd3** are still amorphous oils due to their high branching density (Figures S34–S39). On the other hand, an increase of the temperature from 30°C to 50°C results in a higher activity and branching density but a decreased molecular weight of the products.

A large number of α-diimine palladium catalysts showed effective copolymerization of ethylene with polar monomers due to their functional group tolerance.[4] However, iminopyridyl Pd (II) catalysts for ethylene/polar monomer copolymerization are rarely reported. Generally, the incorporation of polar monomers will dramatically reduce copolymer molecular weight and the catalytic activity. With this in mind, one can envision that the iminopyridyl Pd (II) catalysts will produce lower molecular weight functional cooligomers when the behavior to catalyze ethylene homo-oligomerization has been observed for most of these reported iminopyridyl Pd (II) catalysts. However, compared to ethylene homopolymerization, the molecular weight of the generated ethylene-MA cooligomer or copolymer was only slightly changed except for **Pd3**, which afforded the decreased molecular weight of the copolymer (Table 2, entries 2, 4, 6 vs. Table 3, entries 1, 2, and 3, respectively). Notably, the ethylene-MA copolymer with high molecular weight (approximately 1.0×10^4 g mol^{-1}) was obtained by **Pd3** (Table 3, entry 3, Figures S62 and S63). Thus, the fixation of the phenyl substituents in **Pd3** also played a key role in the generation of high molecular weight ethylene-MA copolymers (Table 3 and Figure S3). Further, high MA incorporation ratios of 3.2%–13.8% for **Pd1–Pd3** were observed (Figures S40–S43). Interestingly, **Pd3** afforded

TABLE 3 Copolymerization of ethylene and MA with Pd (II) catalysts

Entry	Cat.	[MA] (M)	Yield (g)	Act.(10^4)[a]	X_M[b]	M_n[c]	M_n[d]	M_w/M_n[d]	B[e]
1	**Pd1**	1	1.38	0.86	11.4	200	300	1.26	97
2	**Pd2**	1	0.70	0.44	3.2	1,100	2,400	1.42	102
3	**Pd3**	1	1.65	1.03	6.6	7,100	9,600	1.49	86
4	**Pd3**	2	0.44	0.28	13.8	4,700	6,500	1.33	100

Note: Conditions: Pd catalyst (20 µmol), NaBArF (1.5 equiv.), total volume of CH_2Cl_2 and MA: 20 ml, 8 h, 50°C, ethylene (4 atm).

[a] Activity is in unit of 10^4 g mol^{-1} h^{-1}.

[b] X_M = monomer incorp. (mol %).

[c] M_n is in unit of g mol^{-1}, determined by ^1H NMR spectroscopy.

[d] M_n is in unit of g mol^{-1}, determined by GPC in THF at 40°C versus polystyrene standards.

[e] B = branches per 1,000 carbons, branching numbers were determined using ^1H NMR spectroscopy, $B = 1{,}000 \times 2(I_{CH3})/3(I_{CH2+CH} + I_{CH3})$. The branches ending with functional groups are added to the total branches.

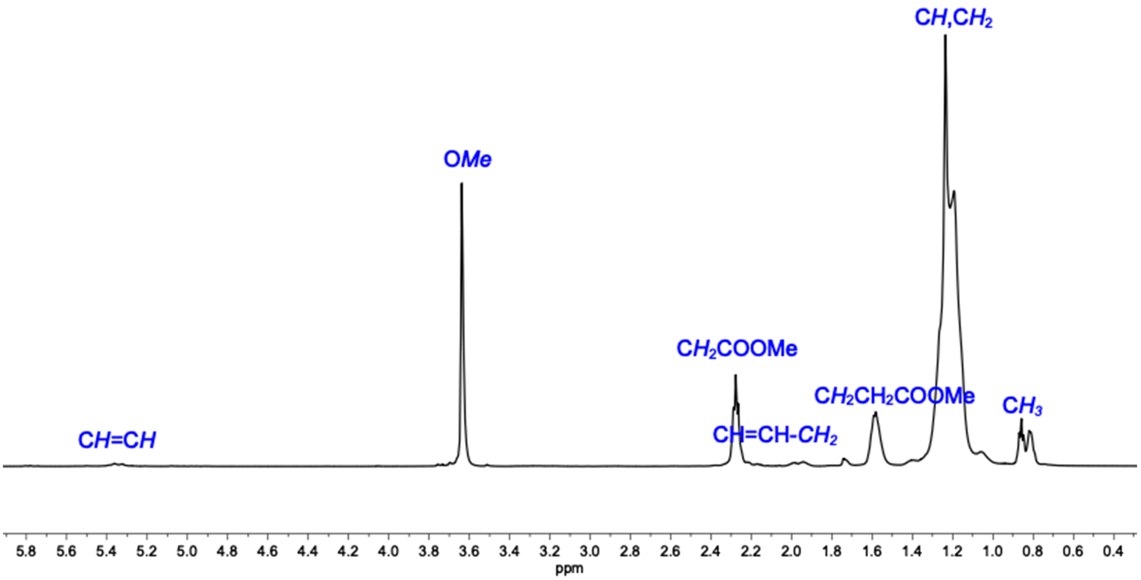


FIGURE 2 ^{1}H NMR spectrum of ethylene-MA copolymer generated by **Pd3** (Table 3, entry 4)

copolymer of up to 13.8% MA incorporation at [MA] = 2.0 M, which did not significantly decrease the molecular weight (M_n = approximately 0.7×10^4 g mol^{-1}) of the obtained copolymer (Figure 2 and Table 3, entry 4). The high efficiency in incorporating MA for these catalysts was most probably attributed to the open coordination space around the pallidum center, which originated from the less axially steric of the pyridine moiety of the asymmetric iminopyridine ligand relative to the symmetric α-diimine ligand. The unique open microenvironment of the iminopyridine ligand would favor MA coordination and subsequent insertion. In addition, the MA units were incorporated predominately at the end of branches (Figure 2), which was consistent with the reported α-diimine Pd (II) catalysts.[2,3,45,46] Similarly, the functional highly branched products obtained in this system are amorphous oils and may find a potential application in the areas of interface active agents or viscosity modifiers.[47]

3 | CONCLUSIONS

In summary, the strategy to increase the molecular weight of polyolefins by introducing the bulky substituents in α-diimine Ni (II) and Pd (II) catalysts has been extensively studied. However, this strategy most often showed no improvement for iminopyridyl Ni (II) and Pd (II) catalysts. Herein, we report the rotation-restricted strategy to synthesize high molecular weight polyethylene or functionalized polyethylene using iminopyridyl Ni (II) and Pd (II) catalysts. The molecular structure of **Ni3** and **Pd3** with the phenyl substituents fixed in the diarylmethyl moiety showed that the rotation-restricted strategy gave access to the proper orientation of bulky substituents and provided effective blockage of the axial positions of the metal center. As a result, **Ni3** and **Pd3** can produce polymers or copolymers with much higher molecular weight than that obtained by other Ni (II) and Pd (II) complexes in ethylene polymerization and copolymerization with MA. Meanwhile, **Pd3** exhibited a high MA incorporation up to 13.8% with only a slightly decrease of the copolymer molecular weight. These results suggested the potential for wide utility of rotation-restricted strategy in developing new late transition metal olefin polymerization catalysts.

4 | EXPERIMENTAL SECTION

4.1 | General considerations

All manipulations were performed in a glovebox or using standard Schlenk techniques. n-Hexane, ether, and toluene were freshly distilled from sodium under N_2. Dichloromethane was dried over P_2O_5 overnight and distilled. Starting reagents for the synthesis of ligands and complexes were purchased and used without purification. The synthetic route for anilines **A2** and **A3** was shown in supporting information. The ligand **L1** and the corresponding nickel complex **Ni1** were synthesized according to the method we previously reported.[15] The palladium precursor (COD) PdMeCl was prepared by using a literature procedure.[48] ^{1}H, ^{13}C NMR spectra were acquired by a Bruker DPX 500 spectrometer or a JEOL JNM-ECZ600R 600 spectrometer at 25°C unless otherwise stated. The chemical shifts were referenced to the residual solvent resonance or SiMe$_4$ signal (0 ppm). ^{1}H NMR spectra of polyethylene produced by **Ni1–Ni3** were obtained on a JEOL JNM-ECZ600R 600 spectrometer at 70°C using C_6D_6 as solvent. Elemental analysis was performed by the Analytical Center of the Anhui University. Mass spectra were determined using electro spray ionization (ESI) LCMS-2010A or Atouflex Speed MALDI-TOF MS. X-ray diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K$^\alpha$ radiation (λ = 0.71073 Å). Molecular weight and molecular weight distribution of the products generated by **Ni1–Ni3** were determined by gel permeation chromatography (GPC) with a PL-220 at 150°C using trichlorobenzene as a solvent, and the system was calibrated using polystyrene standard. Molecular weight and molecular weight distribution of the products obtained by **Pd1–Pd3** were determined by GPC eluting with THF on a Tosh instrument (Tosh, Tokyo, Japan). The system was calibrated with polystyrene standards and operated at 40°C with a flow rate of 0.35 ml/min. Melting transition temperature (T_m) of polymer samples was measured by differential scanning calorimetry (DSC) on an Auto Q20 from TA Instrument. Samples were heated to 150°C under a nitrogen flow (50 ml/min) and kept for 5 min to remove thermal history, then cooled to 40°C at a rate of 10°C/min, and finally reheated to 150°C at the same rate.

4.2 | Synthesis of ligands

L2: 2-Pyridylaldehyde (0.81 g, 7.5 mmol) and the aniline **A2** (1.28 g, 2.5 mmol) were dissolved in anhydrous toluene. Subsequently, a catalytic amount of *p*-methylbenzenesulfonic acid (0.02 g) was added in the solution, and the reaction mixture was refluxed under stirring. After 12 h, the reaction mixture was concentrated and 200 ml methanol was added. The yellow solid precipitated and was separated by filtration. The pure product can be obtained by layering their CH$_2$Cl$_2$ solution with methanol at room temperature. Yield: 1.36 g, 87%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.52 (d, *J* = 4.7 Hz, 1H, N=C-*H*), 7.64 (t, *J* = 6.9 Hz, 1H, Ar-*H*), 7.58 (d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.23 (m, 1H, Ar-*H*), 7.11–7.01 (m, 8H, Ar-*H*), 7.01–6.94 (m, 4H, Ar-*H*), 6.86–6.81 (m, 4H, Ar-*H*), 6.80 (s, 1H, Ar-*H*), 6.51 (s, 2H, Ar-*H*), 5.47 (s, 2H, C*H*Ar$_2$), 2.11 (s, 3H, Ar-CH_3), 1.94 (s, 12H, CH (Ph*Me*)$_2$). ^{13}C NMR (126 MHz, CDCl$_3$) δ 164.36 (N=*C*), 153.98, 149.48, 148.02, 141.78, 136.51, 136.05, 132.61, 132.14, 130.25, 129.74, 128.42, 126.31, 125.65, 124.95, 121.56, 45.87 (*C*HAr$_2$), 21.55 (Ar-*C*H$_3$), 19.27 (CH (Ph*Me*)$_2$). ESI-MS (m/z): Calcd for $C_{43}H_{41}N_2$: 585.3270. Found: 585.3252, [M + H]$^+$. Anal. Calcd for $C_{43}H_{40}N_2$: C, 88.32; H, 6.89; N, 4.79. Found: C, 88.40; H, 6.90; N, 4.77.

L3: The same procedure as above was employed. **L3** was obtained as the yellow solid. Yield: 1.12 g, 77%. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.64 (d, *J* = 4.7 Hz, 1H, N=C-*H*), 7.81–7.71 (m, 2H, Ar-*H*), 7.42–7.34 (m, 2H, Ar-*H*), 7.00 (m, 8H, Ar-*H*), 6.91 (d, *J* = 7.5 Hz, 4H, Ar-*H*), 6.71 (m, 4H, Ar-*H*), 6.66 (s, 2H, Ar-*H*), 5.09 (s, 2H, C*H*Ar$_2$), 3.42–3.30 (m, 4H, Ar-CH_2), 2.68 (m, 4H, Ar-CH_2), 2.10 (s, 3H, Ar-CH_3). ^{13}C NMR (126 MHz, CDCl$_3$) δ 165.90 (N=*C*), 154.15, 149.15, 147.95, 140.62, 139.68, 136.15, 132.26, 131.74, 130.91, 130.46, 129.44, 126.86, 125.75, 125.16, 122.61, 55.77 (*C*HAr$_2$), 31.94 (Ar-*C*H$_2$), 21.48 (Ar-*C*H$_3$). ESI-MS (m/z): Calcd for $C_{43}H_{37}N_2$: 581.2957. Found: 581.2947, [M + H]$^+$. Anal. Calcd for $C_{43}H_{36}N_2$: C, 88.93; H, 6.25; N, 4.82. Found: C, 88.79; H, 6.23; N, 4.78.

4.3 | Synthesis of Ni (II) complexes

Ni2: A mixture of **L2** (0.58 g,1.0 mmol) and anhydrous NiBr$_2$ (0.22 g, 1.0 mmol) was added in dried ethanol (10 ml) under N$_2$. The reaction mixture was refluxed under stirring for 24 h. The solution was allowed to cool to room temperature, and the precipitate was formed. The precipitate was washed with ether (3 × 5 ml) and dried under vacuum to give **Ni2** as orange powder (0.45 g, 56%). MALDI-TOF-MS (m/z): calcd. for $C_{43}H_{40}BrN_2Ni$: 721.1728. Found: 721.1379 [M-Br]$^+$. Anal. Calcd for $C_{43}H_{40}Br_2N_2Ni$: C, 64.29; H, 5.02; N, 3.49. Found: C, 64.33; H, 5.05; N, 3.41.

Ni3: Using a procedure similar to that for the preparation of **Ni2**, **Ni3** was obtained as orange powder (0.68 g, 85%). MALDI-TOF-MS (m/z): calcd. for $C_{43}H_{36}BrN_2Ni$: 717.1415. Found: 717.1409 [M-Br]$^+$. Anal. Calcd for $C_{43}H_{36}Br_2N_2Ni$: C, 64.62; H, 4.54; N, 3.50. Found: C, 64.55; H, 4.57; N, 3.48.

4.4 | Synthesis of Pd (II) complexes

Pd1: To a solution of ligand **L1** (0.58 g, 1.0 mmol) in dry CH$_2$Cl$_2$ (10 ml) was added 0.26 g (COD)PdMeCl (1.0 mmol). The reaction mixture was stirred for 24 h at room temperature. The solvent was concentrated to approximately 2 ml under reduced pressure, and 10 ml n-hexane was added, resulting the formation of the precipitate. The precipitate was washed with n-hexane (3 × 5 ml) and dried under vacuum to give **Pd1** as yellow powder (0.56 g, 76%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 9.10 (d, *J* = 4.5 Hz, 1H, N=C-*H*), 7.72

(td, *J* = 7.8, 1.5 Hz, 1H, Ar-*H*), 7.63–7.54 (m, 1H, Ar-*H*), 7.05 (d, *J* = 7.9 Hz, 4H, Ar-*H*), 6.93 (d, *J* = 8.0 Hz, 4H, Ar-*H*), 6.81 (q, *J* = 8.1 Hz, 8H, Ar-*H*), 6.66 (s, 2H, Ar-*H*), 6.32 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 6.02 (s, 1H, Ar-*H*), 5.77 (s, 2H, C*H*Ar$_2$), 2.31 (s, 6H, CH (Ph*Me*)$_2$), 2.20 (s, 6H, CH (Ph*Me*)$_2$), 2.18 (s, 3H, Ar-C*H*$_3$), 0.99 (s, 3H, Pd-C*H*$_3$). ^{13}C NMR (151 MHz, CDCl$_3$) δ 171.09 (N=*C*), 151.25, 149.42, 142.14, 140.84, 139.36, 137.83, 136.53, 136.38, 136.17, 135.98, 129.67, 129.13, 128.99, 128.96, 128.28, 125.05, 51.34 (*C*HAr$_2$), 21.70 (Ar-*C*H$_3$), 21.17 (CH (Ph*Me*)$_2$), 21.08 (CH (Ph*Me*)$_2$), 1.26 (Pd-*C*H$_3$). MALDI-TOF-MS (m/z): calcd for $C_{43}H_{40}N_2Pd$: 690.2226. Found: 690.0861, [M-Me-Cl]$^+$. Anal. Calcd for $C_{44}H_{43}ClN_2Pd$: C, 71.25 H, 5.84; N, 3.78. Found: C, 71.19; H, 5.83; N, 3.72.

Pd2: Using the same procedure as for the synthesis of **Pd1**, **Pd2** was obtained as a yellow powder (0.53 g, 72%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 9.04 (d, *J* = 4.4 Hz, 1H, N=C-*H*), 7.67 (td, *J* = 7.8, 1.5 Hz, 1H, Ar-*H*), 7.58–7.52 (m, 1H, Ar-*H*), 7.21 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.17–7.14 (m, 2H, Ar-*H*), 7.05 (q, *J* = 6.8 Hz, 4H, Ar-*H*), 6.95 (t, *J* = 7.1 Hz, 2H, Ar-*H*), 6.78 (t, *J* = 7.2 Hz, 4H, Ar-*H*), 6.59 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 6.57 (s, 2H, Ar-*H*), 6.14 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 5.81 (s, 2H, C*H*Ar$_2$), 5.46 (s, 1H, Ar-*H*), 2.39 (s, 6H, CH (Ph*Me*)$_2$), 2.14 (s, 3H, Ar-C*H*$_3$), 1.91 (s, 6H, CH (Ph*Me*)$_2$), 0.94 (s, 3H, Pd-C*H*$_3$). ^{13}C NMR (151 MHz, CDCl$_3$) δ 172.83 (N=*C*), 151.24, 148.76, 144.17, 143.16, 138.12, 137.88, 137.62, 136.89, 136.41, 136.30, 130.76, 130.58, 130.44, 130.37, 128.55, 128.18, 126.94, 126.61, 125.80, 125.77, 125.32, 45.74 (*C*HAr$_2$), 21.68 (Ar-*C*H$_3$), 20.96 (CH (Ph*Me*)$_2$), 19.48 (CH (Ph*Me*)$_2$), 1.64 (Pd-*C*H$_3$). MALDI-TOF-MS (m/z): calcd for $C_{43}H_{40}N_2Pd$: 690.2226. Found: 690.0060, [M-Me-Cl]$^+$. Anal. Calcd for $C_{44}H_{43}ClN_2Pd$: C, 71.25 H, 5.84; N, 3.78. Found: C, 71.19; H, 5.83; N, 3.72.

Pd3: Using the same procedure as for the synthesis of **Pd1**, **Pd3** was obtained as a yellow powder (0.62 g, 84%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 9.22 (d, *J* = 4.7 Hz, 1H, N=C-*H*), 7.77 (td, *J* = 7.7, 1.5 Hz, 1H, Ar-*H*), 7.69–7.64 (m, 1H, Ar-*H*), 7.28 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 7.18–7.12 (m, 4H, Ar-*H*), 7.08 (dd, *J* = 13.1, 7.0 Hz, 4H, Ar-*H*), 6.93 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 6.78–6.73 (m, 4H, Ar-*H*), 6.50 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 6.20 (s, 1H, Ar-*H*), 6.15 (t, *J* = 7.3 Hz, 2H, Ar-*H*), 5.45 (s, 2H, C*H*Ar$_2$), 3.54 (td, *J* = 13.9, 4.8 Hz, 2H, Ar-C*H*$_2$), 3.32 (dt, *J* = 17.5, 3.9 Hz, 2H, Ar-C*H*$_2$), 2.94 (ddd, *J* = 18.1, 13.9, 4.9 Hz, 2H, Ar-C*H*$_2$), 2.46 (dt, *J* = 14.0, 4.2 Hz, 2H, Ar-C*H*$_2$), 2.12 (s, 3H, Ar-C*H*$_3$), 0.81 (s, 3H, Pd-C*H*$_3$). ^{13}C NMR (151 MHz, CDCl$_3$) δ 172.80 (N=*C*), 152.12, 149.17, 143.35, 142.43, 140.30, 138.70, 137.73, 137.37, 134.99, 131.80, 131.73, 131.61, 130.11, 129.09, 128.09, 127.45, 127.17, 126.82, 126.79, 125.87, 55.77 (*C*HAr$_2$), 33.37 (Ar-*C*H$_2$), 30.27 (Ar-*C*H$_2$), 21.93 (Ar-*C*H$_3$), 0.38 (Pd-*C*H$_3$). MALDI-TOF-MS (m/z): calcd for $C_{43}H_{36}N_2Pd$: 686.1913. Found: 686.1448, [M-Me-Cl]$^+$. Anal. Calcd for $C_{44}H_{39}ClN_2Pd$: C, 71.64 H, 5.33; N, 3.80. Found: C, 71.69; H, 5.37; N, 3.77.

4.5 | General procedure for Ni (II)-catalyzed ethylene polymerization

A mechanically stirred 100 ml Parr reactor was heated to 120°C for 1 h under vacuum and then cooled to room temperature. The autoclave was pressurized to 1.1 atm of ethylene and was then charged with 29 ml toluene and 0.4 ml solution of Et_2AlCl in toluene (1 M) at the desired temperature. The system was maintained by continuously stirring for 5 min, and then 1 ml solution of nickel complex in CH_2Cl_2 was injected and the ethylene pressure was increased to 8 atm to initiate polymerization and stirred continuously at appropriate temperature for the desired time. Polymerization was quenched by addition of acidified methanol (5% HCl in MeOH). The product was precipitated in methanol, filtered, and dried under vacuum at 45°C to a constant weight.

4.6 | General procedure for Pd (II)-catalyzed ethylene polymerization

A 350 ml stainless pressure reactor connected with a high-pressure gas line was firstly dried at 90°C under vacuum for 1 h and then cooled to the desired polymerization temperature. The reactor was charged with 38 ml of CH_2Cl_2 and the required amount NaBArF in a glovebox. After equilibration at the desired polymerization temperature for 10 min, the required amount of catalyst in 2 ml of CH_2Cl_2 was injected rapidly into the mixture via syringe. With a rapid stirring, the reactor was pressurized and maintained at 4 atm of ethylene. After 3 h, the pressure reactor was vented and the polymer was dried under vacuum to a constant weight.

4.7 | General procedure for Pd (II)-catalyzed ethylene copolymerization with MA

A 350 ml stainless pressure reactor connected with a high-pressure gas line was firstly dried at 90°C under vacuum for 1 h and then cooled to the desired polymerization temperature. The reactor was charged with the required amount of CH_2Cl_2 and NaBArF in a glovebox. After equilibration at the desired polymerization temperature for 10 min, the required amount of freshly distilled MA and the required amount of catalyst in 2 ml of

CH_2Cl_2 were injected rapidly into the mixture via syringe. With a rapid stirring, the reactor was pressurized and maintained at 4 atm of ethylene. After 8 h, the pressure reactor was vented and the copolymer was dried under vacuum to a constant weight.

ASSOCIATED CONTENT

Supplementary Materials

Full experimental details for the NMR and MS spectra of compounds, NMR, GPC and DSC curves of polymer samples. CCDC numbers of complexes **Ni3** and **Pd3** are **1,985,218** and **1,985,217**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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CONFLICT OF INTEREST

The authors declare no competing financial interests.

AUTHOR CONTRIBUTIONS

Hongwei Peng: Data curation; investigation. **Shuaikang Li:** Data curation; investigation. **Gen Li:** Investigation. **Shengyu Dai:** Conceptualization; formal analysis; resources; supervision. **Mingjun Ji:** Data curation; formal analysis; project administration. **Zhe Liu:** Resources. **Lihua Guo:** Conceptualization; funding acquisition; supervision.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in the supporting information of this article.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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