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Synthesis of Polyethylenes with Controlled Branching with α-Diimine Nickel Catalysts and Revisiting Formation of Long-Chain Branching

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ABSTRACT:

The synthesis of polyethylenes with precise branching, especially long-chain branching (LCB), using ethylene monomer as a single feedstock is of a significant academic and industrial interest. On the basis of the *ortho*-aryl effect, a series of α-diimine nickel complexes with mono-aryl-substituted anilines has been designed and prepared for the synthesis of the polyethylenes with controlled branching. The introduction of the *ortho*-aryl on aniline moieties enhanced the branching control ability of the α-diimine nickel catalysts. A different mechanistic model was proposed to interpret the presence of methyl and LCB but absence of other short branches in the obtained polyethylenes. LCB was formed by ethylene insertion into the primary Ni-alkyl species originating from nickel migration to methyl terminal of the growing chain because of restricted ethylene insertion into secondary Ni-alkyl species with an α-ethyl or a bulkier alkyl group.

Keywords: nickel catalyst, chain walking, ethylene, polyethylene, long-chain branching, controlled branching

INTRODUCTION

The discovery of late transition metal nickel and palladium catalysts has initiated a new olefin polymerization field because it leads to the formation of new polymeric materials, especially α-diimine type catalysts initially reported by Brookhart.[1] A distinguishing feature of α-diimine nickel and palladium catalysts for ethylene polymerization is chain walking, which involves a series of sequential β-hydride eliminations, alkene rotations, and reinsertions that relocates the active metal center along the growing polymer chain.[2] The polyethylenes (PEs) with various types of branching can be synthesized with α-diimine nickel and palladium catalysts by tuning steric and electronic effects and polymerization conditions.[3]

Generally, chain walking produces statistical amounts of the expected branches for α-diimine nickel catalyst systems. The branched PEs obtained by standard α-diimine nickel catalysts contain most of methyl branch (C_1), small amount of ethyl, propyl, and butyl branches (C_2-C_4), trace of amyl branch (C_5), and large amounts of long-chain branching (LCB) ($\geq C_6$).[1a,4] As described mechanistic model by Brookhart, LCB is produced by chain walking involving successive β-H elimination (at least 6 steps) and reinsertion process.[2] Monte-Carlo simulation of branching distribution in α-diimine nickel-catalyzed polyethylenes has showed that branching frequencies decrease steadily from methyl (C_1) to decyl branches (C_{12}), and large amounts of LCB ($\geq C_6$) is a result of sum of hexyl and longer branches.[5] The synthesis of polyethylenes with controlled branching by chain walking mechanism therefore remains a great challenge although precise branching can be used to tune material properties over a wide range, making polyolefins extremely versatile materials.[6] LCB in particular, is nevertheless important because it has a dramatic effect on polymer properties and material processing properties, thereby the synthesis of the long-chain branched polyethylene using ethylene monomer as a single feedstock is of a significant academic and industrial interest.[7]

Numerous studies on ethylene polymerizations using nickel and palladium catalysts have established that the branching density and distribution strongly depend on the nature of the ligand.[1a,4] An effective approach to controlling branching distribution of polyethylene products is the modification of ligand frameworks. For instance, α-diimine nickel catalysts with modified *ortho* substituents afforded methyl-branched polyethylenes by controlling chain walking reaction.[8] The polyethylenes containing high content of LCB were also obtained by nickel catalysts, and the level of LCBs was hardly interpreted by common chain walking mechanism.[9] The alternative mechanisms of LCB formation such as incorporation of long-chain α-olefins or macromonomers and intra- or intermolecular C–H activation were presumably presented.[9a,b,f] Recently, methyl and LCB were merely observed in semicrystalline polyethylenes and ethylene based copolymers by α-diimine palladium catalysts, but no mechanistic model of LCB formation was provided.[10] These contributions shed light on these issues that controlling branching density and distribution of polymeric products in Ni/Pd-catalyzed ethylene polymerization was feasible and the LCB might be formed by various mechanistic models.

Rieger groups have previously reported the "*ortho*-aryl effects" of α-diimine nickel and palladium catalysts, which provide a viable access to controlling polyethylene microstructure by tailor-made coordination geometry.[11] α-Diimine nickel catalysts with *ortho*-aryl substituted anilines are therefore ideal candidates for microstructure control of polyethylenes. In this paper, a series of novel α-diimine nickel complexes with mono-*ortho*-aryl-substituted anilines has been designed for precise synthesis of polyethylenes with methyl and LCB. An attractive mechanistic model of controlled branching is also proposed, which enables researchers to gain greater mechanistic understanding on the LCB formation in Ni/Pd-catalyzed ethylene polymerization.

RESULTS AND DISCUSSION

Synthesis and crystal structure of nickel complexes

α-Diimine ligands with 2,6-unsymmetrically substituted anilines were synthesized by the Schiff base condensation reaction using trimethylaluminum (TMA) as an activator of the corresponding anilines according to our previously reported methods.[12] The α-diimine ligands were obtained as non-statistical stereochemical mixtures because of the existence of geometric (*E*/*E*-, *E*/*Z*-, and *Z*/*Z*-) and conformational (*syn*- and *anti*-) isomers, which was similar to previous observation with related α-diimine compounds.[4a,9d,e,13] α-Diimine nickel complexes with different substituents were obtained by addition of the corresponding ligands to a stirring suspension of (DME)NiBr$_2$ (DME: dimethoxyethane) in CH$_2$Cl$_2$ (Figure 1). An attempt to synthesize the diphenyl α-diimine nickel complex with 2,4-dimethyl-6-naphthyl anilines was unsuccessful under similar conditions. Nickel complex **7** containing unsymmetric aniline moieties was also prepared by two-step condensation reactions and used for comparison.

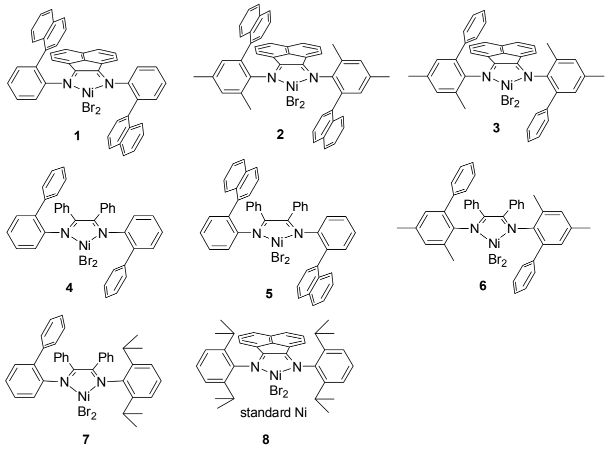


Figure 1. Molecular structures of α-diimine nickel complexes.

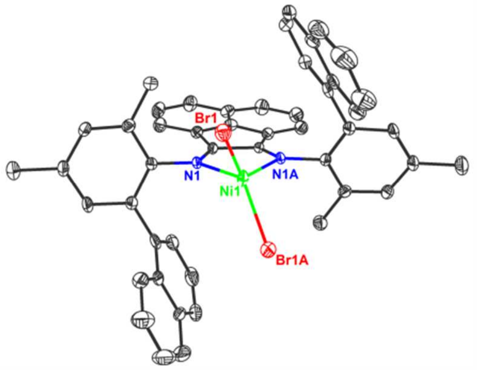


Figure 2. Crystal structure of nickel complex **2** with thermal ellipsoids of 30 % probability. The hydrogen atoms and four CH_2Cl_2 molecules are omitted for clarity.

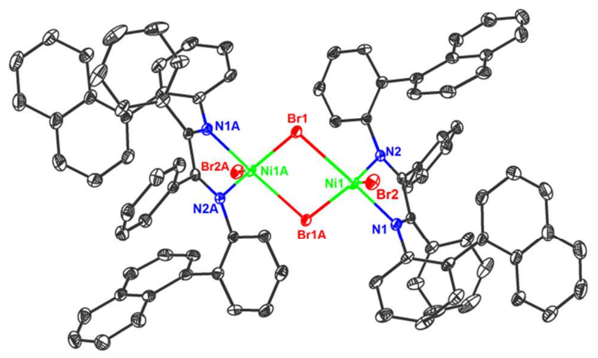


Figure 3. Crystal structure of nickel complex **5** with thermal ellipsoids of 30 % probability. The hydrogen atoms and two CH_2Cl_2 are omitted for clarity.

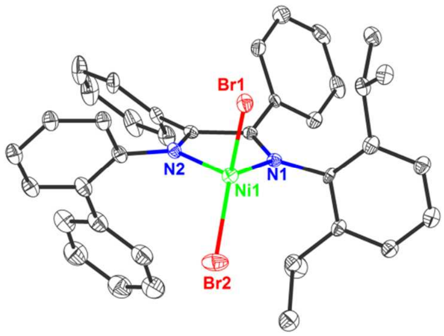


Figure 4. Crystal structure of nickel complex **7** with thermal ellipsoids of 30 % probability. The hydrogen atoms are omitted for clarity.

Single crystals of nickel complexes **2**, **5**, and **7** suitable for X-ray diffraction analysis were obtained by slow evaporation of the nickel complex solutions in CH_2Cl_2 (Figures 2-4). Nickel complexes **2** and **7** adopt a four-coordinate geometry for the nickel center (Figures 2 and 4), whilst the dimerization of complex **5** gives a five-coordinate geometry (Figure 3). Single crystal X-ray diffraction analysis shows that nickel complex **2** is present as a *rac*-isomer and exhibits pseudo C_2-symmetry in the solid state. Both of twist angles between the aniline plane and the naphthyl ring are 64.5^{o}, suggesting that two naphthyl rings provide the unique surrounding space around the nickel center, a feature linked to chain walking.[14]

Ethylene polymerization

Preliminary ethylene polymerizations were carried out using nickel complexes **1-8** after activation with methylaluminoxane (MAO) under 0.5 atm ethylene pressure and 0 °C. Comparisons of polymerization results in Table 1 clearly demonstrated the effects of *ortho* substituent and ligand backbone on ethylene polymerization. For acenaphthyl α-diimine nickel catalysts, increasing the steric bulks of the *ortho* substituent (entries 1 *vs* 3 *vs* 2) led to an increase in polymer molecular weight and polymerization yield, which was well consistent with previous observation.[4a,12a] When two phenyl groups were introduced on the ligand backbone instead of acenaphthyl group, the polymer molecular weight increased (entries 1 *vs* 5 and 3 *vs* 6).

Table 1. Ethylene polymerization results with nickel catalysts **1-8**/MAO at 0 °C. [a]

entry	cat.	yield (g)	M_n [b] (kg/mol)	PDI [b]	T_m [c] (°C)	BD [d] (/1000C)	Me content [e] %
1	**1**	0.82[f]	1.2	1.8	120	0	0
2	**2**	2.87	127.1	2.5	128	4.8	100
3	**3**	1.61	99.5	2.4	126	16.0	100
4	**4**	2.03	7.7	3.3	119,125	14.5	100
5	**5**	2.10[f]	3.1	3.1	114, 121	11.2	100
6	**6**	0.94	180.7	2.0	127	8.5	100
7	**7**	1.93	151.0	2.2	117	24.5	92.0
8	**8**	2.40	224.9	2.9	81	48.1	74.6

[a] Polymerization conditions: 5 μmol of nickel, Al(MAO)/Ni = 600, 30 min, 0.5 atm ethylene pressure, 20 mL toluene. [b] M_n and PDI were determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C using narrow polystyrene standards as calibration. [c] Determined by differential scanning calorimetry (DSC), second heating. [d] Branching density, branches per 1000 carbon atoms determined by ^{1}H NMR spectroscopy. [e] Me content is the mole ratio of the methyl branching in the various branching distributions, determined by ^{13}C NMR spectroscopy. [f] polyethylene wax.

Herein, more attentions were focused on the effects of *ortho* substituent and ligand backbone on the branching structure of the obtained polyethylene including branching density and branching distribution. It was interesting to note that catalysts **1-6** with mono-*ortho*-aryl substituted anilines afforded polyethylenes with much lower branching density than the standard α-diimine nickel catalyst **8** with

2,6-diisopropyl substituents. Similar observations have been reported with an α-diimine palladium catalyst bearing dibenzhydryl ($CH(Ph)_2$) groups and α-diimine nickel catalysts with 2,6-diphenyl substituents for ethylene polymerization.[10,11] Reducing branching density by introducing *o*-aryl substituted aniline could be reasonably attributed to the "*ortho*-aryl effect" proposed by Rieger.[11]

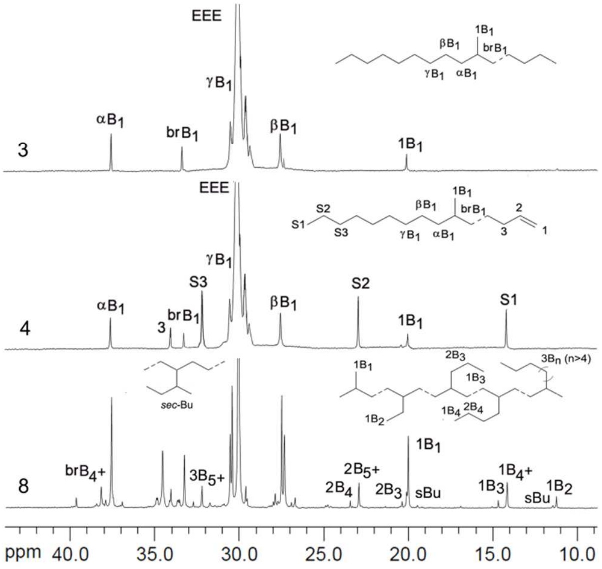


Figure 5. ^{13}C NMR spectra of polyethylenes produced by catalysts **3, 4,** and **8** (doubt bond singles are omitted for **4**) (entries 3, 4, 8 in Table 1).

To gain deep insight into definitive microstructure of the polyethylenes, investigations using ^{13}C NMR spectroscopy were further undertaken (Figure 5). The branching distributions were quantitatively calculated on the basis of previous resonance assignments.[15] Surprisingly, only methyl (19.99 ppm, $1B_1$) was present in the polyethylenes produced by catalysts **2-6** and other branching such as ethyl, propyl, butyl, amyl, and LCB were not detected with the exception of the fully linear polyethylene obtained by catalyst **1** (Table 1). For low-molecular-weight polyethylenes obtained by catalysts **1**, **4**, and **5**, the resonances at 32.04, 22.75, 13.99

ppm were assigned to the end group of the polyethylene chain rather than LCB (Figure 5).[16] This assignment was further supported by the observation of the double bond of the chain end at 139.05, 114.12 ppm (Figures S1 in Supporting Information).[15] This result strongly indicated that *ortho*-aryl substituents also affected branching distribution, besides branching density of polyethylenes.

Table 2. Characterization of polyethylenes obtained by **2**, **3**, **6-8**/MAO. [a]

entry	cat.	P (atm)	T (°C)	yield (g)	M_n [b]	PDI [b]	T_m [c] (°C)	BD [d]	branching distribution (mol%)[e]					
									Me	Et	Pr	Bu	Am	LCB
2	**2**	0.5	0	2.87	127.1	2.5	128	4.8	100	0	0	0	0	0
9	**2**	0.5	20	1.37	78.1	2.5	118	6.0	100	0	0	0	0	0
10	**2**	0.5	40	1.29	30.8	3.0	112	20.5	81.5	0	0	0	0	18.5
11	**2**	0.5	60	1.20	21.1	2.1	97, 109	31.9	60.7	4.6	0	0	0	34.8
12	**2**	10	0	6.65	174.3	2.9	137	0	0	0	0	0	0	0
13	**2**	10	20	7.12	125.7	2.5	136	0	0	0	0	0	0	0
14	**2**	10	40	7.78	60.3	2.7	120	8.3	93.9	0	0	0	0	6.1
15	**2**	10	60	10.35	36.2	2.4	114	22.9	65.8	0	0	0	0	34.2
3	**3**	0.5	0	1.61	99.5	2.4	126	16.0	100	0	0	0	0	0
16	**3**	0.5	20	1.77	50.5	2.3	99	41.3	89.9	0	0	0	0	10.1
17	**3**	0.5	40	1.60	9.7	4.2	–[f]	93.7	77.1	2.4	0.8	0	0	19.7
18	**3**	0.5	60	1.12	4.9	4.5	–[f]	125.3	65.4	6.1	2.1	4.0	0.9	21.5
6	**6**	0.5	0	0.94	180.7	2.0	127	8.5	100	0	0	0	0	0
19	**6**	0.5	20	1.41	126.1	1.9	92	43.0	88.1	0	0	0	0	11.9
20	**6**	0.5	40	1.02	87.8	1.7	–[f]	100.3	84.2	1.8	0	0	0	14.0
21	**6**	0.5	60	0.87	73.4	1.8	–[f]	123.9	75.8	4.8	1.6	1.5	0	16.3
7	**7**	0.5	0	1.93	151.0	2.2	117	24.5	92.0	8.0	0	0	0	0
22	**7**	0.5	20	2.46	98.2	2.3	87	48.7	75.9	2.3	2.3	1.7	0.7	17.1
23	**7**	0.5	40	1.21	61.8	2.4	–[d]	105.7	72.8	2.9	2.3	2.2	0.8	19.0
8	**8**	0.5	0	2.40	224.9	2.9	81	48.1	74.6	5.9	4.1	2.8	2.8	9.8

[a] Polymerization conditions: 5 μmol of nickel, Al(MAO)/Ni = 600, 30 min, 20 mL toluene; 100 mL toluene for high pressure polymerization of 10 atm (entries 12-15). [b]

in unit of kg/mol, M_n and PDI were determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C using narrow polystyrene standards as calibration. [c] Determined by differential scanning calorimetry (DSC), second heating. [d] Branching density, branches per 1000 carbon atoms determined by ^{1}H NMR spectroscopy. [e] Branching distribution is the mole ratio of the desired branching in the various branching distributions, determined by ^{13}C NMR spectroscopy. [f] Not determined.

Commonly, the branching structure of the polyethylene obtained by α-diimine nickel catalysts is sensitive to polymerization temperature and ethylene pressure. Nickel catalysts **2**, **3**, and **6** were selected to investigate the influences of reaction temperature and ethylene pressure on the polymer branching structure (Table 2), considering that the obtained high-molecular-weight polyethylenes could eliminate the effect of the chain end group on LCB calculation. As previously reported, increasing temperature also led to a remarkable increase in branching density in a range of temperature from 0 to 60 °C for catalysts **2**, **3**, and **6**.[4a]

Notably, ^{13}C NMR analysis showed that the order of branching presence could not follow branching length order with an increase in temperature. For polyethylenes obtained by catalysts **3** and **6** with 2,4-dimethyl-6-phenyl anilines, only methyl was observed at 0 °C. When the temperature was increased to 20 °C, only methyl and LCB appeared and other short branches including ethyl, propyl, butyl, and amyl branches were not present (Table 2 and Figures S4 and S6 in Supporting Information). The intensive CH_3 peak at 14.09 ppm was typical for butyl or longer branches ($1B_{4+}$). The existence of LCB and the exclusion of butyl branch were further supported by the absence of a signal at 23.39 ppm, which was characteristic for butyl branch ($2B_4$).

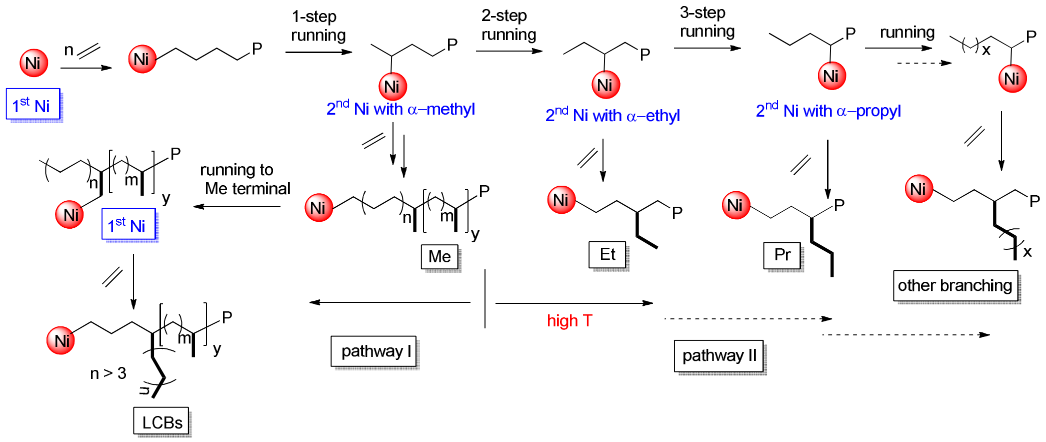
Additionally, the methine (CH) signal at 38.15 ppm of LCB on the main chain (brB$_{4+}$) was also detected.[15] Additional ethyl branch appeared in the polyethylene at temperatures up to 40 °C. Further increasing temperature to 60 °C, all branches were clearly detected in the ^{13}C NMR spectroscopy (Figures S4 and S6 in supporting information). Compared with catalysts **3** and **6**, catalyst **2** with the installation of 6-naphthyl groups instead of 6-phenyl groups also followed the same trend but showed better controlled behavior. Propyl, butyl, and amyl branches were not present in the polyethylene obtained by catalyst **2** at 60 °C (entries 11). When the ethylene pressure was increased from 0.5 to 10 atm, the branching density decreased and branching distribution was more facilely controlled. Only methyl and LCB were observed for the polyethylenes obtained by catalyst **2** in a range of temperature from 0 to 60 °C (entries 12-15).

In comparison, α-diimine nickel catalysts with mono-*ortho*-aryl substituents showed better control behavior for polyethylene branching structure than standard α-diimine nickel catalyst **8** with 2,6-alkyl substituents (entry 8 in Table 2). Catalyst **2** also showed comparable branching selectivity to previously reported α-diimine nickel catalysts. For example, α-diimine nickel catalysts bearing 2,6-diaryl aniline moieties reported by Rieger produced polyethylenes with relatively low branching density of 3-48/1000C, and predominant methyl, LCB and trace of ethyl were observed in the formed polyethylenes.[11] The cyclophane derived α-diimine catalyst reported by Guan produced the polyethylenes with higher branching density (66-96/1000C) as compared to the Rieger's catalyst. The obtained PEs contained short chain branches with most being simple methyl branches.[3b] The “sandwich” α-diimine nickel catalyst reported by Brookhart and Daugulis produced highly branched polyethylenes (up to 152/1000C) containing most of methyl branching.[17] α-Diimine nickel catalysts bearing dibenzhydryl ($CH(Ph)_2$) anilines developed by Long afforded moderately branched polyethylenes (63-75/1000C), and branching contents consisted of both methyl branching and LCB even at high temperatures.[18] Dibenzobarrelene derived *α*-diimine nickel catalyst with 4-methyl-2-(1-(2,4,6-trimethylphenyl) ethyl)aniline moieties reported by Coates catalyzed ethylene polymerization to form lowly branched polyethylenes (1-63/1000C), and branching density decreased with increasing ethylene pressure and reducing temperature.[14] Precise control of the polyethylene branching structure, especially branching distribution, became possible by the introduction of mono-*ortho*-aryl on aniline moieties on α-diimine ligands. This behavior could be attributed to the unique coordination geometry of α-diimine nickel complexes with mono-*ortho*-aryl-anilines. Our claim was further supported by experimental results of ethylene polymerization using an unsymmetrical α-diimine nickel catalyst **7** with 2,6-diisopropyl and 2-phenyl anilines. For the polyethylenes obtained by catalyst **7**, the order of branching presence followed branching length order with an increase in temperature and all of branches were clearly detected in the ^{13}C NMR spectroscopies above 20 °C (entries 22, 23), which was similar to the observation using standard α-diimine nickel catalyst **8** (entry 8).[15a]

Mechanistic studies of LCB formation

In principle, branches on the polyethylenes produced by α-diimine nickel and palladium catalysts are believed to form by the migration of metal center along the growing chain. This chain walking process occurs via β-hydrogen elimination generating a metal-hydride olefin species, followed by 2,1-reinsetion with opposite regiochemistry. Coordination and insertion of an ethylene monomer result in a methyl branch. An additional chain-walking step followed by ethylene insertion produces an ethyl branch. Further chain walking results in the formation of longer branches (pathway II in Scheme 1).[4a] Therefore, the order of branching presence follows branching length order.

For the polyethylenes with controlled branching structure obtained by α-diimine nickel catalysts, a crucial question, the branching formation mechanism, remains unanswered. Methyl branch placed in the polyethylene samples in the present work is reasonably interpreted by the chain walking mechanism. However, LCB is unlikely attributed to the previously reported chain walking process because of absence of other short-chain branches in the polyethylene samples produced by our nickel catalyst systems. Some researchers have noted similar observations using other nickel catalysts, and an alternative mechanism of LCB formation by incorporation of long-chain α-olefins or macromonomers has been speculated.[9a,b] This incorporation mechanism has precedent in early transition metal-catalyzed olefin polymerization (Ti, Zr, and Hf based catalysts), but is hardly operated for nickel and palladium catalysts because insertion of α-olefins into nickel and palladium active center generally leads to 1,ω- or 2,ω- enchainment by chain straightening.[19,20] Intra- or intermolecular C-H activation has been presumably presented in iminophosphonamide nickel-catalyzed-ethylene polymerization,[9f] but authors also note that it is not clear why the formation of long-chain branches (> C_6) is favored over other intramolecular C-H activation reactions. As a matter of fact, the most common and presumably strongest interaction between nickel and palladium metal centers and the alkyl group is the β-agostic interaction.[4a]



Scheme 1. Proposed mechanistic model for the formation of LCB.

We herein provide an attractive mechanism for LCB formation in these polyethylene materials. As shown in Scheme 1, methyl branch is formed by chain walking process involving one-step β-H elimination followed by ethylene insertion. Two-step chain walking involving successive twice β-hydrogen elimination followed by 2,1-reinsetion leads to the generation of a secondary Ni-alkyl species with an α-ethyl, but ethyl branch cannot form because of no occurrence of ethylene insertion. As a result, nickel active center further migrates on the polyethylene chain. Analogously, propyl, butyl, amyl, and LCB cannot also be formed because the secondary Ni-alkyl species possesses bulkier substituents. Therefore, the methyl branched polyethylene growing chain is formed in the initial time. When nickel metal migrates to methyl terminal by successive multiple-step chain walking on the methyl branched polyethylene growing chain, a primary Ni-alkyl species is produced. LCB is formed when ethylene inserts into the primary Ni-alkyl species (pathway I in Scheme 1).

In the proposed mechanism, it is a crucial point that ethylene insertion into a secondary Ni-alkyl species with an α-ethyl or a bulkier alkyl cannot occur at lower temperatures (pathway II in in Scheme 1). Therefore, a mechanistic question remains. Why does ethylene merely insert into the primary Ni-alkyl species or the secondary Ni-alkyl species with an α-methyl? The reasons could be attributed to steric interactions because *ortho*-aryl substituted anilines provided unique enclosed surrounding space around nickel metal center. Brookhart has previously reported that 1-hexene can merely insert into secondary nickel-alkyl species with an α-methyl for the α-diimine nickel catalyst with mono-*tert*-butyl substituted anilines, and insertion of 1-hexene into secondary nickel-alkyl species with bulkier groups such as ethyl and propyl groups cannot occur.[17] The restricted insertion of α-olefin into primary Ni-alkyl species or secondary nickel-alkyl species with an α-methyl has been commonly observed using nickel catalysts with two 2,6-diisopropylaniline moieties under the adopted conditions.[20] Regioselective 2,1-insertion and precision chain walking have also been observed in “sandwich” α-diimine nickel catalyzed-α-olefins polymerizations.[17] Coates has recently performed a detailed study on the insertion pathways and chain straightening mechanisms of “sandwich” α-diimine nickel catalysts for α-olefin polymerizations using ^{13}C-labeling technique.[21] The positions of the nickel species prior to the next monomer insertion are mostly located at the primary chain end position, the previously installed methyl terminal, and the penultimate chain end position. Osakada also reported that the α-diimine palladium catalyst with 2,4-dimethyl-6-phenylanilines polymerized 4-alkylcyclopentenes to produce the polymers with the higher isotacticity than the standard palladium catalyst with 2,6-diisopropylanilines because of steric repulsion.[22] Therefore, the restricted insertion of ethylene into primary Ni-alkyl species or secondary nickel-alkyl species with an α-methyl is presumably reasonable by design of coordination geometry.

Analogously, ethylene insertion into a secondary Ni-alkyl species does not occur in the pathway I. Probably, no ethylene insertions take place until nickel center migrates the final destination at the previously installed methyl terminal to form a primary Ni-alkyl species. According to the proposed mechanism, LCB should be always accompanied with methyl branching on the branched polyethylene chain. The experimental results of branching distribution in Table 2 further support this claim. For the obtained polyethylenes by catalyst **2** under 10 atm ethylene pressure and low temperatures (entries 12 and 13 in Table 2), LCB is also not formed when methyl branching is not produced.

The proposed mechanistic model can also reasonably explain the effect of temperature on branching structure. Increasing temperature leads to more strong walking ability of nickel species, thereby nickel species migrates to methyl terminal more readily and LCB forms with higher frequency at elevated temperature. Further increasing temperature leads to the presence of other short branching, which is a result of two-step or multiple-step chain walking followed by insertion of ethylene (pathway II in Scheme 1) because the ethylene insertion into the secondary nickel-alkyl species with an α-ethyl or a bulkier alkyl is favored energetically at high temperature.[19] When temperature is increased to a critical value, LCB is formed by two pathways including ethylene insertion into the primary Ni-alkyl species arising from nickel migration to methyl terminal (pathway I) and ethylene insertion into the secondary Ni-alkyl species ($> C_6$) by multiple-step chain walking (pathway II).

In contrast to previous work on the formation of LCB, our study provides a novel mechanistic model. We believe that the proposed mechanistic model can reasonably interpret high content of LCB in the polyethylenes obtained by other nickel catalysts.[9,17,18] Besides, LCB formation by the proposed mechanism (pathway I) may be not fully excluded for polyethylenes obtained by previously reported α-diimine nickel catalysts with *ortho* alkyl substituents. [4a]

CONCLUSIONS

In summary, we have reported α-diimine nickel catalysts with the mono-aryl-substituted anilines that afford the polyethylenes with precise branching. The introduction of the *ortho*-aryl on aniline moieties remarkably enhanced the branching control ability of the α-diimine nickel catalysts. The polyethylenes with precise branching including methyl and LCB were synthesized and polymer molecular weight could be tuned by varying ligand substituents. Mechanistic study showed that methyl was produced by one-step chain walking whilst LCB was formed by ethylene insertion into the primary Ni-alkyl species originating from nickel migration to methyl terminal because of restricted ethylene insertion into the secondary Ni-alkyl species with an α-ethyl or a bulkier alkyl. The novel mechanistic model (pathway I) is helpful in revisiting the LCB formation obtained by nickel catalysts and enables researchers to gain greater mechanistic understanding on branching formation in Ni/Pd-catalyzed ethylene polymerization.

EXPERIMENTAL SECTION

General Procedures

All manipulations involving air- and moisture sensitive compounds were performed under dried and purified nitrogen (99.999%) using standard vacuum-line, Schlenk, or dry glovebox techniques.

Materials

Toluene and hexane were distilled from Na/K alloy before being used. Dichloromethane was distilled from CaH_2 under nitrogen atmosphere. 2-Phenylaniline, 2-bromotoluene, 1-bromonaphthalene, trimethyl borate, tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$), 2-bromoaniline and 2-bromo-4,6-dimethylanilne, acenaphthenequinone, benzil, phenylboronic acid, and 1-naphthylboronic acid were purchased from Alfa Aesar Chemical and used as received. 2,6-Diisopropylaniline were purchased from Aldrich Chemical and were distilled under reduced pressure before use. Trimethylaluminium (1M, hexane) were purchased from Aldrich Chemical and used as received. Methylaluminoxane (MAO) solution (10 wt. % in toluene) was purchased from Acros. Ethylene (99.99%) was purified by passing through Agilent moisture and oxygen traps. Other commercially available reagents were purchased and used without purification. A standard acenaphthyl α-diimine nickel complex with 2,6-diisopropylaniline was synthesized according to the literature.

Measurements

Elemental analyses were performed on a Vario EL microanalyzer. Mass spectra were obtained using electro spray ionization (ESI) LCMS-2010A for organic compounds. Matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) were performed on Bruker ultrafleXtreme for nickel complexes. NMR spectra of organic compounds were carried out on a Varian Mercury-Plus 300 MHz spectrometer in $CDCl_3$ using TMS as a reference. ^{13}C NMR spectra of polymers were carried out on a Bruker 500 MHz at 120 °C. Sample solutions of the polymer were prepared in o-$C_6H_4Cl_2$/o-$C_6D_4Cl_2$ (50% v/v) in a 10 mm sample tube. The spectra of the quantitative ^{13}C NMR were taken with a 74° flip angle, an acquisition time of 1.5 s, and a delay of 4.0 s. DSC analyses were conducted with a Perkin Elmer DCS-7 system. The DSC curves were recorded at second heating curves at a heating rate of 10 °C/min and a cooling rate of 10 °C/min. GPC analysis of the molecular weights and molecular weight distributions (PDI = M_w/M_n) of the polymers at 150 °C were performed on a PL-GPC 220 high-temperature chromatograph equipped with a differential refractive-index detector. 1,2,4-Trichlorobenzene (TCB) was used as the eluent at a flow rate of 1.0 mL/min.

Crystal structure determination

The crystal of nickel complex was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. Data obtained with the ω-2θ scan mode was collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Cu K_α radiation (λ= 1.54178 Å). The structure of nickel complexes was solved by direct methods using the program *SHELXS97*, while further refinement with full-matrix least squares against F^2 was obtained with the *SHELXL97* program package. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Ethylene polymerization at atmosphere pressure

A round-bottom Schlenk flask with stirring bar was heated for 3 h at 150 °C under vacuum and then cooled to room temperature. The Schlenk flask was pressurized to 0.5 atm of ethylene pressure (gage pressure) and vented three times. The appropriate MAO solution and toluene were added into the glass reactor under 0.5 atm of ethylene. Toluene and 2 mL of a solution of nickel complex were added sequentially by syringe to the well-stirred solution, and the total reaction volume was kept at 20 mL. The ethylene pressure was kept constant at 0.5 atm by continuous feeding of ethylene throughout the polymerization reaction. The reaction temperatures were controlled with an external oil bath or a cooler in polymerization experiments. The polymerizations were terminated by the addition of 200 mL of acidic methanol (95:5 methanol/HCl) after continuously stirring for an appropriate period. The resulting precipitated polymers were collected and treated by filtration, washed with methanol several times, and dried in vacuum at 60 °C to a constant weight.

Ethylene polymerization at high pressure

A mechanically stirred 300 mL Parr reactor was heated to 150 °C for 2 h under vacuum and then cooled to room temperature. The autoclave was pressurized to 2 atm of ethylene and vented three times. The autoclave was then charged with solution of MAO in toluene under 0.5 atm of ethylene at initialization temperature. After continuously stirring for an appropriate period, 2 mL solution of nickel complex and toluene solvent were charged into the autoclave under 0.5 atm of ethylene and the total reaction volume was kept at 100 mL. The ethylene pressure was raised to 10 atm. The reaction temperature was controlled by means of a heater or cooler and found to be ± 2 °C as monitored by an internal thermocouple. The reaction was carried out for 30 min. Polymerization was terminated by addition of acidic methanol after releasing ethylene pressure. The resulting precipitated polymers were collected and treated by filtering, washed with methanol several times, and dried under vacuum at 60 °C to a constant weight.

Synthesis of substituted aniline

Synthesis of 2-naphthyl-aniline (1a)

In a 250 mL Schlenk flask, $Pd(PPh_3)_4$ (0.3 mmol, 340 mg) and 2-bromoaniline (23.5 mmol, 4.04 g) were dissolved in 80 mL toluene. Ethanol solution (30 mL) of 1-naphthylboronic acid (40 mmol, 6.88 g) and an aqueous solution K_2CO_3 (100 mmol, 13.8 g) were added under nitrogen atmosphere. The reaction mixture was refluxed for

3 days, then the organic layer was separated and the aqueous phase was extracted with ether. After dried over $MgSO_4$ and evaporated solvents, the mixtures were purified by column chromatography on silica gel using petroleum ether/ethyl acetate (4:1) as eluent. The final product was crystallized from petroleum ether as white solid in 87.4% yield. ^{1}H NMR (300 MHz, $CDCl_3$): 7.87-6.83 (m, 11H, phenyl and naphthyl), 2.90 (s, 2H, NH_2). EI-MS (m/z): 220 $[M]^+$.

Synthesis of 2,4-dimethyl-6-naphthyl-aniline (2a)

The synthesis of compound **2a** was carried out as described for **1a**, the white solid was in 82.3% yield. ^{1}H NMR (300MHz, $CDCl_3$): 7.90 (t, 2H, Ar), 7.66 (d, 1H, Ar), 7.58-7.41(m, 3H, Ar), 7.02 (s, 2H, Ar), 6.89 (s, 1H, Ar), 3.13 (s, 2H, NH_2), 2.32 (s, 3H, CH_3), 2.27 (s, 3H, CH_3). EI-MS (m/z): 248 $[M]^+$.

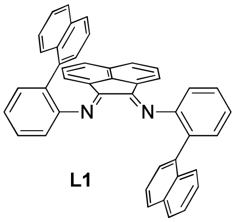
Synthesis of 2,4-dimethyl-6-phenyl-aniline (3a)

The synthesis of compound **3a** was carried out as described for **1a**, phenylboronic acid was used instead of 1-naphthylboronic acid. The white solid was in 74.2%. ^{1}H NMR (300 MHz, $CDCl_3$): 7.57-6.90 (m, 7H, Ar-H), 3.10 (s, 2H, NH_2)), 2.25 (s, 3H, CH_3), 2.17 (s, 3H, CH_3). EI-MS (m/z): 198 $[M]^+$.

Synthesis of α-diimine ligands

Synthesis of L1 Ar–N=C(An)–(An)C=N–Ar (An = acenaphthyl, Ar = 2-naphthyl-phenyl)

Under a nitrogen atmosphere, trimethylaluminum (8 mL, 1.0 M in hexane) was slowly injected into 2-naphthyl-aniline 1.752 g (8 mmol) in toluene (20 mL) solution at room temperature, and then the reaction system was heated to reflux for 2 h. After the solution was cooled to room temperature, acenaphthenequinone (0.612 g, 3.36 mmol) was added into the reaction Schlenk flask. The mixture was continuously stirred for 6 h at refluxing temperature. When the solution was cooled to room temperature, the reaction mixture was hydrolyzed with 5% aqueous NaOH solution. The organic product was extracted with ethyl acetate and dried over $MgSO_4$, and the solvent was evaporated off. The desired product was obtained by recrystallization from ethanol as orange crystal in 75.3% yield. Three isomers were detected in a solution according to ^{13}C NMR spectrum. ^{1}H NMR (300 MHz, $CDCl_3$): 7.80-6.87 (m, 28H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): 160.19 (*C*=N), 157.24 (*C*=N), 156.34 (*C*=N), 150.20 (*C*–N), 149.46 (*C*–N), 148.78 (*C*–N), 140.81, 140.05, 138.21, 136.90, 136.20, 133.89, 133.45, 133.33, 133.17, 133.04, 132.09, 131.95, 131.74, 131.19, 130.63, 130.35, 130.22, 129.39, 129.23, 129.00, 128.63, 128.57, 128.36, 128.23, 127.79, 127.74, 127.70, 127.55, 127.49, 127.46, 127.30, 127.16, 126.95, 126.90, 126.02, 125.27, 125.12, 125.00, 124.74, 124.68, 124.39, 123.69, 123.26, 122.90, 122.48, 122.36, 119.07, 118.27, 117.37. Anal. Calcd for $C_{44}H_{28}N_2$: C: 90.38, H: 4.83, N: 4.79%. Found: C: 89.91, H: 4.74, N: 4.77%.

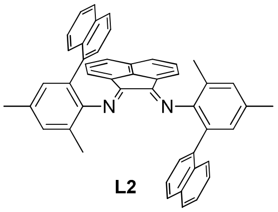


L1

Synthesis of L2 Ar–N=C(An)–(An)C=N–Ar (An = acenaphthyl, Ar = 2,4-dimethyl-6-naphthyl-phenyl)

A similar synthesis method as **L1**, the orange crystal was obtained in 86.4% yield.

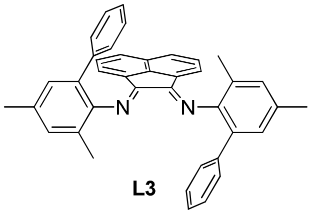
Three isomers were detected with a ratio of 5.0 : 2.5 : 1. ^{1}H NMR (300 MHz, $CDCl_3$): 7.95-6.70 (m, 24H, Ar-H), 2.42 (s, 6H, CH_3, major + middle isomers), 2.35 (m, 6H, CH_3, minor isomer), 2.25 (s, 3H, CH_3, minor isomer), 2.14 (s, 3H, CH_3, minor isomer), 2.09 (s, 3H, CH_3, major isomer), 1.94 (s, 3H, CH_3, major isomer), 1.62 (s, 3H, CH_3, middle isomer), 1.47 (s, 3H, CH_3, middle isomer). ^{13}C NMR (75 MHz, $CDCl_3$): 160.65 (C=N), 146.34, 139.92, 137.20, 136.54, 133.57, 133.15, 132.02, 132.39, 133.22, 131.51, 131.26, 130.61, 130.53, 130.31, 130.17, 129.87, 129.75, 128.67, 128.54, 128.32, 127.96, 127.71, 127.36, 127.03, 126.87, 126.64, 126.60, 125.98, 125.74, 125.65, 125.52, 125.41, 125.35, 124.71, 124.51, 124.38, 123.89, 122.82, 122.76, 122.66, 122.59, 122.47, 122.33, 20.96 (CH_3-Ar), 18.16 (CH_3-Ar), 17.84 (CH_3-Ar), 17.52 (CH_3-Ar). Anal. Calcd for $C_{48}H_{36}N_2$: C: 89.97, H: 5.66, N: 4.37%. Found: C: 89.94, H: 5.68, N: 4.31%.



L2

Synthesis of L3 Ar–N=C(An)–(An)C=N–Ar (An = acenaphthyl, Ar = 2,4-dimethyl-6-phenyl-phenyl)

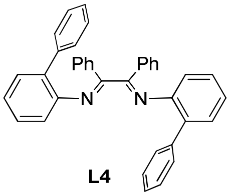
A similar synthesis method as **L1**, the orange crystal was obtained in 84.1% yield. Two isomers were detected with a ratio of 0.35 : 1. ^{1}H NMR (300 MHz, $CDCl_3$): 7.78 (s, 1H, Ar-H, minor isomer), 7.76 (s, 1H, Ar-H, minor isomer), 7.74 (s, 1H, Ar-H, major isomer), 7.71 (s, 1H, Ar-H, major isomer), 7.49-7.46 (m, 4H, Ar-H, minor + major isomer), 7.37-7.27 (m, 2H, Ar-H, minor + major isomers), 7.14-7.01 (m, 8H, Ar-H, minor + major isomers), 6.80 (s, 1H, Ar-H, minor isomer), 6.77 (s, 1H, Ar-H, minor isomer), 6.73 (s, 1H, Ar-H, major isomer), 6.70 (s, 1H, Ar-H, major isomer), 2.46 (s, 6H, CH_3, major isomer), 2.45 (s, 6H, CH_3, minor isomer), 2.11 (s, 6H, CH_3, major + minor isomers). ^{13}C NMR (75 MHz, $CDCl_3$): 160.91 (*C*=N, minor isomer), 160.42 (*C*=N, major isomer), 145.63 (major isomer), 142.69 (minor isomer), 140.48 (major isomer), 140.41 (minor isomer), 139.66 (minor isomer), 139.59 (major isomer), 133.44 (major isomer), 133.28 (minor isomer), 131.75 (minor isomer), 130.73 (minor isomer), 130.62 (major isomer), 130.49 (minor isomer), 130.33 (minor isomer), 129.82 (major isomer), 129.57 (minor isomer), 129.46 (major isomer), 129.30 (major isomer), 129.13 (minor isomer), 129.05 (minor isomer), 128.99 (minor isomer), 128.82 (major isomer), 128.62 (major isomer), 128.55 (minor isomer), 128.46 (major isomer), 127.84 (minor isomer), 127.83 (major isomer), 127.65 (minor isomer), 127.64 (major isomer), 127.37 (major isomer), 126.22 (major isomer), 125.91 (major isomer), 125.23 (minor isomer), 122.54 (minor isomer), 122.43 (major isomer), 20.91 (*C*H_3, major isomer), 20.86 (*C*H_3, minor isomer), 18.03 (*C*H_3, minor isomer), 17.95 (*C*H_3, major isomer). Anal. Calcd for $C_{40}H_{32}N_2$: C: 88.85, H: 5.97, N: 5.18%. Found: C: 88.72, H: 5.84, N: 5.10%.



L3

Synthesis of ligand L4 Ar–N=C(An)–(An)C=N–Ar (An = phenyl, Ar = 2-phenyl-phenyl)

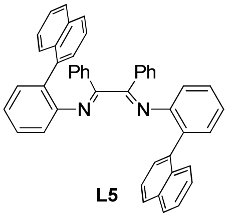
A similar synthesis method as **L1**, the orange crystal was obtained in 65.1% yield. ^{1}H NMR (300 MHz, CDCl$_3$): 7.57 (d, 4H, Ar-H), 7.34 (m, 3H, Ar-H), 7.22-7.20 (m, 5H, Ar-H), 7.16-7.11 (m, 6H, Ar-H), 7.05-7.00 (m, 3H, Ar-H), 6.87-6.82 (m, 5H, Ar-H), 6.44 (d, 2H, Ar-H). ^{13}C NMR (75 MHz, CDCl$_3$): 162.70 (*C*=N), 145.70 (*C*–N), 139.24, 137.51, 134.70, 130.49, 130.19, 129.56, 128.51, 128.16, 127.30, 127.24, 126.21, 125.66, 118.23. Anal. Calcd for $C_{38}H_{28}N_2$: C: 89.03, H: 5.51, N: 5.46%. Found: C: 88.78, H: 5.46, N: 5.34%.



L4

Synthesis of L5 Ar–N=C(An)–(An)C=N–Ar (An = phenyl, Ar = 2-naphthyl-phenyl)

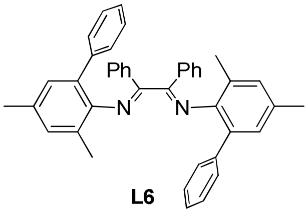
A similar synthesis method as **L1**, the orange crystal was obtained in 71.4% yield. ^{1}H and ^{13}C NMR spectroscopies of ligand **L5** were very complex because of appearance of geometric and conformational isomers. ^{1}H NMR (300 MHz, CDCl$_3$): 7.96-6.27 (m, 32H, Ar-H). ^{13}C NMR (75 MHz, CDCl$_3$): 164.16 (*C*=N), 161.75 (*C*=N), 148.14, 147.74, 146.75, 146.75, 144.16, 137.59, 137.18, 136.84, 136.0-124.72 (br, m), 123.94-123.35 (br), 120.9, 120.12, 118.35, 118.16, 115.18. Anal. Calcd for $C_{46}H_{32}N_2$: C: 90.16, H: 5.26, N: 4.57%. Found: C: 89.73, H: 5.13, N: 4.46%.



L5

Synthesis of L6 Ar–N=C(An)–(An)C=N–Ar (An = phenyl, Ar = 2,4-dimethyl-6-phenyl-phenyl)

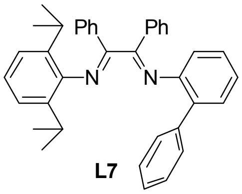
A similar synthesis method as **L1**, the orange crystal was obtained in 58.1% yield. Two isomers were detected with a ratio of 4.3:1. ^{1}H NMR (300MHz, $CDCl_3$): 7.49-6.12 (m, 24H, Ar-H, major + minor isomers), 2.33-2.16 (m, 9H, CH_3, major isomer), 2.06 (s, 6H, CH_3, minor isomer), 1.30 (s, 3H, CH_3, minor isomer), 1.06 (s, 3H, CH_3, major isomer), 0.90 (s, 3H, CH_3, minor isomer). ^{13}C NMR (75 MHz, $CDCl_3$): 164.07 (*C*=N), 161.86 (*C*=N), 144.18, 143.88, 140.50, 140.04, 137.00, 132.86, 132.47, 130.97, 130.51, 129.89, 129.69, 129.60, 129.43, 129.16, 128.54, 128.22, 128.08, 127.94, 127.68, 127.55, 127.05, 126.93, 126.61, 126.07, 125.97, 124.06, 20.75 (CH_3), 19.35 (CH_3), 18.94 (CH_3), 18.72 (CH_3), 16.73 (CH_3). Anal. Calcd for $C_{42}H_{36}N_2$: C: 88.69, H: 6.38, N: 4.93%. Found: C: 88.51, H: 6.32, N: 4.76%.



L6

Synthesis of L7 Ar^1–N=C(R)–(R)C=N–Ar^2 (R = phenyl, Ar^1 = 2-phenyl-phenyl, Ar^1 = 2,6-diisopropylphenyl)

Ligand **L7** was synthesized by two step condensation reactions of α-dione compounds with various anilines.



L7

Benzil (1.05 g, 5.0 mmol) and 2,6- diisopropylaniline (0.95 mL, 5.0 mmol) were charged in a round bottom flak with acetic acid (100 mL), and then the reaction system was heated to reflux. After 8 h, the reaction mixture was cooled to room temperature overnight. The yellow crystal was collected and treated by filtration, washed with ethanol several times, and dried under vacuum. The mono-condensation product was produced in 89.6% yield. ^{1}H NMR (300 MHz, $CDCl_3$): 8.15-7.91 (m, 2H, Ar-H), 7.59-7.10 (m, 9H, Ar-H), 6.88 (s, 2H, Ar-H), 2.87 (hept, 2H, $C\mathit{H}(CH_3)_2$), 1.06 (d, 6H, $CH(C\mathit{H}_3)_2$), 0.96 (d, 6H, $CH(C\mathit{H}_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$): 196.57 (*C*=O), 165.22 (*C*=N), 144.60 (*C*–N), 136.16, 135.02, 133.54, 131.44, 130.05, 128.75, 128.43, 127.82, 124.03, 123.31, 122.17, 28.45 ($\mathit{C}H(CH_3)_2$), 24.10 ($\mathit{C}H_3$), 21.22 ($\mathit{C}H_3$). Elemental analysis calculated for $C_{26}H_{27}NO$: C, 84.51; H, 7.37; N, 3.79%. Found: C, 84.38; H, 7.26; N, 3.61%.

The second step condensation reaction was carried out according to a similar synthesis method as **L1.** The mono-condensation product was used instead of α-dione compounds, and 1 equiv. 2-phenyl-aniline was used. The desired product was obtained as orange crystal in 68.7 % yield. Three isomers were detected with a ratio of 1 : 2.3 : 3.4. ^{1}H NMR (300 MHz, $CDCl_3$): 7.93-6.38 (m, 22H, Ar-H, minor + middle + major isomers), 2.88 (m, 2H, $C\mathit{H}(CH_3)_2$, minor isomer), 2.64 (m, 2H, $C\mathit{H}(CH_3)_2$, middle isomer), 2.51 (m, 2H, $C\mathit{H}(CH_3)_2$, major isomer). 1.26-1.21(m, $C\mathit{H}_3$, 12H, minor isomer), 0.96-0.69 (m, $C\mathit{H}_3$, 12H, middle + major isomers). ^{13}C NMR (75

MHz, $CDCl_3$): 165.82 (C=N), 163.85 (C=N), 162.77 (C=N), 147.47, 144.54, 140.03, 139.59, 137.64, 136.51, 135.88, 135.09, 134.30, 131.93, 130.42, 129.90, 129.39, 128.59, 128.43, 128.19, 127.86, 127.61, 127.36, 127.25, 126.67, 126.46, 124.34, 123.84, 123.53, 123.32, 121.77, 121.05, 119.41, 28.73 ($CH(CH_3)_2$), 28.48 ($CH(CH_3)_2$), 28.05 ($CH(CH_3)_2$), 24.35 (CH_3), 23.30 (CH_3), 22.88 (CH_3), 20.54 (CH_3). Anal. Calcd for $C_{38}H_{36}N_2$: C, 87.65; H, 6.97; N, 5.38%. Found: C, 87.52; H, 6.85; N, 5.27%.

Synthesis of α-diimine nickel complexes

Synthesis of nickel complex 1

Ligand **L1** (584.2 mg, 1.0 mmol) and $(DME)NiBr_2$ (308 mg, 1.0 mmol) were combined in a Schlenk tube with 20 mL dried dichloromethane, and the reaction mixture was then stirred for 12 h at ambient temperature. The solution was filtered through Celite, and the solvent of the filtrate was removed in vacuum. The residue was recrystallized from dichloromethane/hexane to give nickel complex **1** as red-brown solid in 83.4 % yield. MALDI-TOF-MS (*m*/*z*): 722, 723, 724, 725, $[M\text{-}Br]^+$; 642, 643, 644, 645, $[M\text{-}2Br]^+$; 584, 585, 586, $[M\text{-}NiBr_2]^+$. Anal. Calcd for $C_{44}H_{28}Br_2N_2Ni$: C: 65.80, H: 3.51, N: 3.49%. Found: C: 65.62, H: 3.75, N: 3.45%.

Synthesis of nickel complex 2

Following the above described procedure, the reaction of $(DME)NiBr_2$ and **L2** gave complex **2** in 81.7 % yield. MALDI-TOF-MS (*m*/*z*): m/z: 777, 779, 780, 781, 782, $[M\text{-}Br]^+$; 698, 699, 700, 701, 702, $[M\text{-}2Br]^+$; 640, 641, 642, 643, $[M\text{-}NiBr_2]^+$. Anal. Calcd for $C_{48}H_{36}Br_2N_2Ni$: C: 67.09, H: 4.22, N: 3.26%. Found: C: 66.94, H:

4.10, N: 3.07%.

Synthesis of nickel complex 3

Following the above described procedure, the reaction of (DME)NiBr$_2$ and **L3** gave complex **3** in 78.8 % yield. MALDI-TOF-MS (*m*/*z*): 677, 679, 681, [M-Br]$^+$; 597, 598, 599, 601, [M-2Br]$^+$; 540, 541, 542, [M-NiBr$_2$]$^+$. Anal. Calcd for $C_{40}H_{32}Br_2N_2Ni$: C: 63.28, H: 4.25, N: 3.69%. Found: C: 63.19, H: 4.01, N: 3.45%.

Synthesis of nickel complex 4

Following the above described procedure, the reaction of (DME)NiBr$_2$ and **L4** gave complex **4** in 91.4 % yield. MALDI-TOF-MS (*m*/*z*): 649, 650, 651, 652, [M-Br]$^+$; 570, 571, 572, 573, 574, [M-2Br]$^+$; 512, 513, 514, [M-NiBr$_2$]$^+$. Anal. Calcd for $C_{38}H_{28}Br_2N_2Ni$: C: 62.42, H: 3.86, N: 3.83%. Found: C: 62.18, H: 3.68, N: 3.60%.

Synthesis of nickel complex 5

Following the above described procedure, the reaction of (DME)NiBr$_2$ and **L5** gave complex **5** in 84.0 % yield. MALDI-TOF-MS (*m*/*z*): 750, 751, 752, 753, [M-Br]$^+$; 670, 671, 672, 673, 674, [M-2Br]$^+$; 612, 613, 614, [M-NiBr$_2$]$^+$. Anal. Calcd for $C_{46}H_{32}Br_2N_2Ni$: C: 66.46, H: 3.88, N: 3.37%. Found: C: 66.22, H: 3.73, N: 3.18%.

Synthesis of nickel complex 6

Following the above described procedure, the reaction of (DME)NiBr$_2$ and **L6** gave complex **6** in 71.5% yield. FAB$^+$-MS: m/z: 706, 707, 709, [M-Br]$^+$; 626, 627, 628, 629, [M-2Br]$^+$; 567, 568, 569, 570, 571, [M-NiBr$_2$]$^+$. Elemental analysis calculated for $C_{42}H_{36}Br_2N_2Ni$: C: 64.08, H: 4.61, N: 3.56%. Found: C: 63.95, H: 4.54, N: 3.57%.

Synthesis of nickel complex 7

Following the above described procedure, the reaction of (DME)$NiBr_2$ and **L7** gave complex **7** in 72.1 % yield. MALDI-TOF-MS (*m*/*z*): 658, 659, 660, 661, $[M\text{-}Br]^+$; 578, 579, 580, 581, 582, $[M\text{-}2Br]^+$; 520, 521, 522, $[M\text{-}NiBr_2]^+$. Anal. Calcd for $C_{38}H_{36}Br_2N_2Ni$: C: 61.74, H: 4.91, N: 3.79 %. Found: C: 61.32, H: 5.07, N: 3.54%.

ASSOCIATED CONTENT

Support Information

Crystallographic data, NMR spectra of ligands, and ^{13}C NMR of polymers and assignments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Graphic Abstract

Synthesis of Polyethylenes with Controlled Branching with α-Diimine Nickel Catalysts and Revisiting Formation of Long-Chain Branching

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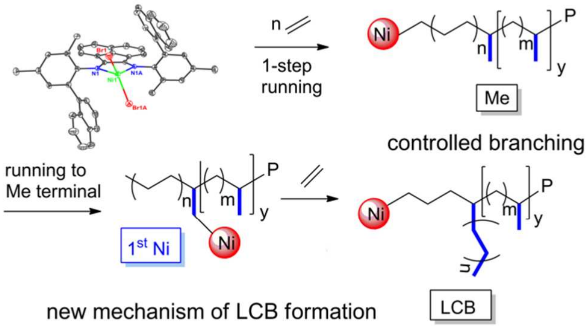

Long-chain branching (LCB) was formed by ethylene insertion into the primary Ni-alkyl species originating from nickel migration to methyl terminal of the growing chain.