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Effects of backbone substituent and intra-ligand hydrogen bonding interaction on ethylene polymerizations with α -diimine nickel catalysts



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ABSTRACT

The design of transition metal catalysts and the development of new catalyst design strategies for olefin polymerization have received substantial attention in the field of polyolefin research. In this paper, we initially reported backbone substituent effects on ethylene polymerizations with α -diimine nickel catalysts and intra-ligand hydrogen bonding interactions operating ethylene polymerizations. A series of α -diimine nickel catalysts with electron-donating/withdrawing groups (OMe, H, Cl, Br, and I) on the dibenzobarrelene backbone were synthesized and employed in ethylene polymerization. Halogen substituents simultaneously showed steric and electronic effects on ethylene polymerization, and catalyst **5** with diiodo (I) substituent showed the highest activity and produced the highest molecular weight polyethylene. The intra-ligand hydrogen bonding interactions (C—H…OMe) were initially observed in the methoxy-substituted dibenzobarrelene α -diimine nickel complex, and the weak noncovalent interactions enhanced the catalyst thermal stability and living fashion of ethylene polymerization at high temperatures up to 80 °C.

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1. Introduction

Olefin polymerization catalysts offer an effective means to control microstructural variations in the molecular architecture of polyolefins [1-4]. The design of new transition metal catalysts and the modification of the reported catalysts not only allow the fine-tuning of the chemical environment around the metal center, but also advance the development of new polyolefin materials [1,5-15]. Two common approaches, including steric and electronic effects, are usually applied to modify transition metal catalysts to enhance catalytic performance and tune the architecture of polyolefins. For example, the α -diimine nickel and palladium catalysts discovered by Brookhart and coworkers have received intensive attention as a staple of late-transition metal catalysts [16-35]. Over the past decades, numerous studies have focused on steric and electronic modifications of the aniline moieties of the α -diimine catalyst to improve catalytic performance, such as thermostability, activity, and tolerance towards polar monomers [36-55].

The demand of bulk *ortho*-aryl substituents is a crucial factor for blocking axial space and suppressing of chain transfer and catalyst deactivation, which contributes to thermostable catalysts and high molecular weight products [1,10-15]. Therefore, a tremendous

* Corresponding author. *E-mail address:* gaohy@mail.sysu.edu.cn (H. Gao). amount of effort has been made to sterically modify the orthoaryl substituents of α -diimine ligands. A representative sample is the α -diimine nickel and palladium catalysts bearing dibenzhydryl (CH(Ph)₂) groups recently reported by Long, Sun, and Chen groups [36-41]. The electronic modification of aniline moieties of α diimine nickel and palladium catalysts can also perturb the electronic environment around the metal center, thereby having a significant influence on olefin polymerizations [18-21,44-48]. Commonly, the increased positive charge of the metal center by the introduction of electron-withdrawing substituents is favorable for olefin coordination and insertion, thereby improving catalytic activity. On the other hand, the introduction of electronwithdrawing groups causes poor catalyst stability and easy deactivation of the catalyst, thus leading to declining activity. Therefore, the design and development of robust nickel and palladium catalysts by electronic modification is highly challenging because of the competition between these two factors [18-20].

In comparison with modifications of aniline moieties, modifications of the ligand backbone are far less intensive and extensive, especially electronic modification of the ligand backbone [43,56-63]. Our work has addressed a promising steric effect of the ligand backbone on the α -diimine-Ni/Pd-catalyzed (co)polymerization of ethylene and polar monomers [57-60]. However, the electronic effect of the ligand backbone in catalyst design has not been systematically studied. Few investigations of the electronic effect of



ligand backbone (4-fluorophenyl and methoxy-substituted acenaphthyl) on ethylene polymerization with α -diimine Ni/Pd catalysts have been reported [18,24,56]. It remains a great challenge to modify the ligand backbone from electronic effect because the installation of electron-withdrawing groups on the α -diimine ligand backbone improves the difficulty of catalyst synthesis.

In addition to steric and electronic modification approaches, weak noncovalent interactions are also employed in modulating catalytic olefin polymerization [27,28,64-84]. The typical hydrogen bonding interaction between hydrogen (H) and an electronegative atom such as fluorine (F) has been observed between the ligand and growing polymer chain [64-71]. A series of phenoxy-imine titanium complexes (Fig. 1A) with ortho-fluoro aryls reported by Fujita and Coates showed living character for ethylene and propylene polymerizations, and the hydrogen bonding interaction between the *ortho*-F and the β -H of the growing polymer chain (C–H...F) could inhibit chain transfer and had been well accepted as an explanation for living polymerizations of ethylene and propylene [64,65,76,77]. In addition, the weak noncovalent interaction between the metal and the heteroatom of the ligand was also observed (Fig. 1B) [27,28]. For fluoro-substituted cyclophanebased α -diimine palladium catalysts, a Pd. . . F interaction stabilized 14-electron alkyl intermediates, thereby suppressing chain transfer processes involving β -H elimination [27]. A second coordination-sphere strategy was developed to modulate olefin (co)polymerizations [80,81]. Chen reported a series of α -diimine



Fig. 1. The proposed weak noncovalent interactions in catalytic olefin polymerizations.

nickel and palladium catalysts bearing nitrogen-containing second coordination spheres for (co)polymerizations of ethylene. Facile metal-nitrogen interactions greatly reduced polymer branching densities in both nickel and palladium catalysts. Higher stability, greater tolerance towards polar groups, and a wider range of polar monomers were realized in the α -diimine palladium system [80]. Installing a polyethylene glycol moiety was also used to facilitate the (co)polymerizations of ethylene (Fig. 1C) [82-84]. The introduction of the polyethylene glycol unit on phosphine sulfonate-based palladium and nickel catalysts significantly enhanced the (co)polymerizations of ethylene and polar monomers because of the ligand-comonomer interaction [83]. In principle, there is a fourth type of weak noncovalent interaction within different parts of a ligand (intra-ligand), but no intra-ligand interaction has been reported in olefin polymerization (Fig. 1D) to the best of our knowledge.

Inspired by the significant enhancement of the dibenzobarrelene backbone on α -diimine Ni/Pd-catalyzed ethylene polymerization [59,60], we sequentially paid attention to the substituent effects of the dibenzobarrelene backbone on ethylene polymerization. In this contribution, a series of α -diimine nickel catalysts with electron-donating/withdrawing groups (OMe, H, Cl, Br, and I) on the dibenzobarrelene backbone were designed and employed in ethylene polymerization. Strikingly, the steric and electronic effects of the dihalo substituent were shown to simultaneously impact ethylene polymerization. The unprecedented intra-ligand interactions (C—H…OMe) were initially observed in the methoxysubstituted dibenzobarrelene α -diimine nickel complex (Fig. 1D), and these weak noncovalent interactions enhanced the catalyst thermal stability and living fashion of ethylene polymerization at high temperatures up to 80 °C.

2. Results and discussion

We previously reported the synthesis and characterization of dibenzobarrelene α -diimine nickel complex **2** [59]. Herein, 1.5disubstituted dibenzobarrelene α -diimine nickel complexes with electron-donating methoxy (OMe) and electron-withdrawing halogen groups were originally designed on the basis of electronic effects (Scheme 1). These substituents were installed on the anthracene from 1,5-disubstituted-anthracene-9,10-dione as raw materials according to reported methods (Scheme S1 in supporting information) [85-89]. 1,5-Disubstituted-9,10-dihydro-9,10-etha noanthracene-11,12-dione compounds were prepared by Diels-Alder addition of 1,5-disubstituted anthracene with vinylene carbonate, hydrolysis, and Swern oxidation reactions using modified literature procedures [90,91]. Corresponding α -diimine ligands were obtained by condensation reactions in high yields. The target α -diimine nickel complexes were synthesized by the reaction of corresponding α -diimine ligands and (DME)NiBr₂ (DME: dimethoxyethane) in CH₂Cl₂. An attempt to synthesize α -diimine nickel complex containing difluoro (F) substituent on the dibenzobarrelene backbone was unsuccessful because the strong electronwithdrawing effect of fluoro groups caused easy decomposition of the nickel complex [92]. In fact, nickel complexes 3 (X = Cl) and 4 (X = Br) also showed relatively poor stability in solution, and the solution color gradually turned light yellow from red beyond 24 h under a nitrogen atmosphere.

Single crystals of two nickel complexes **1** and **5** suitable for Xray diffraction analysis were obtained by slow diffusion of the nickel complex solution in CH₂Cl₂. Similar to the typical structure of α -diimine nickel complexes, two nickel complexes display a distorted tetrahedral geometry (Figs. 2 and 3). The N–Ni–N bite angle of the nickel complex is a crucial factor, which is closely related to the ethylene polymerization property. Interestingly, the steric



Scheme 1. Synthetic routes of α -diimine nickel complexes 1–5.



Fig. 2. Crystal structure of α -diimine nickel complex 1 (X = OMe) with thermal ellipsoids of 30% probability (front and side views).



Fig. 3. Crystal structure of α -diimine nickel complex 5 (X = I) with thermal ellipsoids of 30% probability (front and side views).

effect of substituents has an influence on the N—Ni—N bite angle of the nickel complex (Table 1). Nickel complex **2** without substituents has a bite angle of 78.51° [59], while nickel complexes **1** and **5** have larger bite angles of 81.45° and 82.1°, respectively.

Increasing the N–Ni–N bite angle of the nickel complex by installing 1,5-disubstituents can be attributed to a similar well-known Thorpe-Ingold effect between two nitrogen donor atoms [93]. Besides, the introduction of substituents influences the N–Ni bond

 Table 1

 Crystal parameters regard to the substituent effect of nickel complexes.

Ni complex	Substituent X	N—Ni—N bite angle/°	N—Ni bond length/Å		
1	OMe	81.45 (7)	2.0280(18)/2.0545(18)		
2	H	78.51 (8)	2.133(2)/2.0923(19)		
5	I	82.1 (2)	2.049(6)/2.059(6)		

length of nickel complexes (Table 1), which is associated with complex stability. The N—Ni bond lengths of diiodo substituted complex 5 (2.049/2.059 Å) are shorter than those of complex 2 without substituents (2.133/2.0923 Å), which further supports the steric effect of the substituents. Complex 1 with electron-donating methoxy groups has the shortest N—Ni bond length (2.0280/2.0545 Å), which is reasonably attributed to the electronic effect of the substituents. This result indicates that the introduction of electron-donating groups on the ligand backbone can enhance the stability of the nickel complex, which is consistent with the above observation for the stability of nickel complex in solution.

More strikingly, the introduction of methoxy groups on the dibenzobarrelene backbone leads to noncovalent hydrogen bonding interactions. The distances between the oxygen atoms of methoxy groups and the hydrogen atoms of the isopropyl CH(CH₃) groups are 2.6581 Å for $O_1 \dots H_{11A}$ and 2.9315 Å for $O_2 \dots H_{42A}$, strongly indicating the existence of two intramolecular interactions by O...H hydrogen bonds in nickel complex 1 (Fig. 2). An attempt to prove the existence of these hydrogen bonds in solution of α -diimine nickel complex **1** by ¹H NMR evidence was impractical due to its paramagnetism. Fortunately, single crystal of ligand L1 were also obtained and ORTEP diagram was given in Fig. 4. Noncovalent hydrogen bonding interactions are also present in ligand L1 on the basis of the distances between oxygen atoms and hydrogen atoms of the isopropyl CH(CH₃) groups of 2.8855 Å and 3.0866 Å. ¹H NMR analysis of ligands showed that the methyl protons of the halogenated ligands (L3-L5, X = Cl, Br, I) (1.39-1.20, 1.17-1.04, and 1.08–0.95 ppm) shifted to the downfield relative to those of ligand L2 (X = H) (1.05 and 1.02 ppm) because of the electronwithdrawing effect. However, the methyl protons of the ligand L1 with the electron-donating methoxy groups also shifted to the downfield (1.21–0.96 ppm). This contrast observation was safely attributed to hydrogen bonding interactions between oxygen atoms and hydrogen atoms of the isopropyl groups, strongly supporting that these hydrogen bonds existed in both solution and solid. Previously, the rigid framework of the cyclophane-based nickel complex designed by Guan was reported to enhance thermal stability by prohibiting free rotation of the *N*-aryl bonds [52]. As an alternative approach, the intramolecular hydrogen bonding interaction can restrict rotation of the *N*-aryl bonds and lock the perpendicular-coordination plane conformation of the α -diimine nickel complex, thereby being anticipated to enhance the thermal stability of the catalyst [52,59].

To address the substituent effects of the dibenzobarrelene backbone on ethylene polymerization, α -diimine nickel complexes **1** and **3–5** were activated by Et₂AlCl in a temperature range from 20 to 80 °C (Table 2). An atmospheric ethylene pressure of 1.2 atm was selected because encapsulation of the nickel species into the precipitated high-molecular-weight polymer produced at high ethylene pressure impacts the evaluation reliability. Ethylene polymerizations with catalyst **2** (X = H) were previously reported by our group and are herein listed in Table 2 as comparisons [59].

Under the same polymerization temperatures, catalyst **1** with electron-donating methoxy groups showed lower activities than catalyst 2 without a substituent. However, catalysts 3-5 with electron-withdrawing halogen groups were more active than catalyst 2. The electronic effect of substituents also had the same influence on the molecular weight of the obtained polyethylenes. These results were ascribed to the decreased positive charge of the nickel center by introduction of electron-donating substituents on the dibenzobarrelene backbone. The low positive charge of the metal center was unfavorable for olefin coordination and insertion, thereby reducing the chain growth rate and decreasing the catalytic activity as well as the polymer molecular weight. Although the electronic effect impacted polymerization activity and polymer molecular weight, all of the obtained polyethylenes had narrow polydispersity and catalysts 1-5 showed a living fashion. This result indicated that the chain transfer reaction was hardly affected by the electronic effect of the substituents and the steric effect predominantly determined the chain transfer reaction.

It is well known that the electronegativity order of halogen groups is Cl > Br > I. However, the introduction of halogen groups on the dibenzobarrelene backbone led to a contrary activity trend (**3**(Cl) < **4**(Br) < **5**(I)), which was not reasonably interpreted by the electronic effect mentioned above. Diiodo substituted catalyst **5** showed the highest activity and produced the highest molecular weight polyethylene although iodo substituent had the lowest electronegativity. This unprecedented halogen effect of the dibenzobarrelene backbone on α -diimine-nickel-catalyzed ethylene polymerization was a result of the steric effect. The iodo substituent had the largest atomic size among the three halogens, thereby showing the bulkiest steric hindrance. Increasing the steric bulk on the dibenzobarrelene backbone enhanced the catalytic activity of the nickel catalyst [59], and the atomic size of halogen



Fig. 4. Crystal structure of ligand L1 (X = MeO) with thermal ellipsoids of 30% probability (front and side views).

Table 2						
Ethylene	polymerization	results	using	nickel	catalysts	1–5. ^a

Entry	Ni	Х	T(°C)	Yield (mg)	Activity ^b	M_n^{c} (kg/mol)	PDI ^c	BD ^d (/1000C)
1	1	OMe	20	111	111	101	1.03	91
2	1	OMe	35	147	147	112	1.03	93
3	1	OMe	50	212	212	149	1.04	96
4	1	OMe	65	193	193	130	1.04	98
5	1	OMe	80	166	166	124	1.03	100
6	2	Н	20	182	182	110	1.20	84
7	2	Н	35	248	248	136	1.16	87
8	2	Н	50	281	281	156	1.09	93
9	2	Н	65	261	261	131	1.07	97
10	2	Н	80	trace	-	-	-	-
11	3	Cl	20	219	219	147	1.11	87
12	3	Cl	35	262	262	153	1.09	94
13	3	Cl	50	283	283	190	1.03	98
14	3	Cl	65	274	274	176	1.04	100
15	3	Cl	80	205	205	146	1.08	102
16	4	Br	20	228	228	192	1.18	87
17	4	Br	35	282	282	208	1.11	95
18	4	Br	50	349	349	261	1.06	101
19	4	Br	65	312	312	219	1.05	102
20	4	Br	80	199	199	151	1.11	107
21	5	Ι	20	239	239	238	1.17	89
22	5	Ι	35	401	401	262	1.16	98
23	5	I	50	560	560	308	1.07	104
24	5	I	65	423	423	259	1.09	105
25	5	Ι	80	238	238	170	1.10	107

^a Polymerization conditions: 2 µmol of nickel, Et₂AlCl as cocatalyst, Al/Ni = 600, 1.2 atm ethylene pressure, 30 min, 20 mL toluene and 1 mL CH₂Cl₂.

^b Activity in kg PE/(mol Ni·h).

^c M_n and PDI were determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C.

^d Branching density, branches per 1000 carbon atoms determined by ¹H NMR spectroscopy.

was consistent with the activity order of the dihalo substituted catalysts. The crystal structure data mentioned above showed that diiodo substituted nickel complex **5** had a larger N—Ni—N bite angle, suggesting that the nickel center was deeply surrounded by more crowded space.

To further verify the steric effect of the halogen groups, we pursued a quantitative calculation of the space-filling capabilities of nickel centers using Cavallo's SambVca 2.0 program [94]. Topographic steric maps were used to visualize catalytic pockets around the nickel metal center to show the effect of backbone substituents on the steric hindrance. As shown in Fig. 5, the buried volume of four nickel complexes calculated by X-ray single crystal data consistently increased with an increase in steric bulk on the ligand backbone [95,96]. Nickel complex 2 without a substituent had the smallest buried volume of 45.3, and the introduction of methoxy groups improved the buried volume of the nickel complex (1: 46.6). In combination with the activity order (2 > 1), the electronic effect of methoxy groups dominated the catalytic activity for ethylene polymerization. Nickel complex 2a with 2,6-di-tert-butyl groups reported by our groups was also used for comparison [59]. Indeed, the introduction of 2,6-di-tert-butyl groups on the dibenzobarrelene backbone improved the buried volume of the nickel complex (2a: 47.6). This calculation result was in good agreement with reported experimental results of ethylene polymerization and demonstrated the calculation reliability of the space-filling capabilities [59]. Diiodo-substituted nickel complex **5** had the largest buried volume of 49.6, indicating a steric effect of the iodo substituent and crowded catalytic pockets around the nickel metal center. The iodo substituent showed bulkier steric hindrance around the nickel center than the tert-butyl group, which might be a result of different substituent positions. 1,5-Disubstituents placed on the dibenzobarrelene backbone were more closed to the aniline moieties than 2.6-disubstituents. thereby perturbating steric effect of aniline moieties.

The development of thermally stable olefin polymerization catalysts is of significant interest for industrial gas-phase olefin polymerizations. For α -diimine nickel catalysts, the utilization of *N*-aryl moieties containing steric bulk has been reported to increase their thermal stability by restricting rotation of the *N*-aryl bonds [1,10-15]. The substituent effect of the dibenzobarrelene backbone on the thermal stability of the catalyst was evaluated in a temperature range from 20 to 80 °C under atmospheric pressure. As shown in Table 2, all nickel catalysts showed the same temperature influence on polymerization activity and exhibited the highest activity at 50 °C. A further increase in temperature from 50 °C led to a decrease in catalytic activity. At a high temperature of 80 °C, disubstituted catalysts 1 and 3-5 still showed moderate activities, while catalyst **2** without substituents produced traces of polymer. This result indicated that the introduction of groups with either electron-donating or electron-withdrawing effects on the dibenzobarrelene backbone enhanced the thermal stability of the α diimine nickel catalysts. Usually, it was reported that the installation of electron-donating groups improved catalyst stability [18,19]; enhanced catalyst stability by the introduction of electron-withdrawing halogen groups was herein ascribed to the steric effect on the basis of the buried volume analysis mentioned above.

Additionally, it was noteworthy that the declining percentage of activity was dependent on the steric effect of the substituents, which was closely related to the intramolecular interactions by O...H hydrogen bonds. With increased temperatures from 50 to 80 °C, the activity of catalyst **1** with electron-donating methoxy groups decreased slightly while the activity of catalyst **5** with electron-withdrawing diiodo substituent dropped sharply. The activity of catalyst **1** decreased only by 9% at 65 °C and by 14% at 80 °C from the highest level, whereas the activity of catalyst **5** dropped by 25% at 65 °C and by 44% at 80 °C. This result indicated that catalyst **1** (X = OMe) showed better thermal tolerance than catalyst **5** (X = I). The molecular weight and polydispersity of polyethylenes obtained at high temperatures further supported this claim. With increasing temperature from 50 to 80 °C, the molecular weight of the polyethylenes produced by catalyst **1**



Fig. 5. Topographical steric maps and percent buried volume (%V_{bur}) of α-diimine nickel complexes bearing various substituents on the ligand backbone.

decreased slightly, and the polydispersity (PDI) was nearly invariable and narrow (PDI = \sim 1.04). In contrast, a remarkable decline in polymer molecular weight was observed for catalyst **5**, and the polydispersity became slightly broad (PDI = \sim 1.10) with increasing temperature.

The ethylene polymerization at different time periods ranging from 15 to 90 min was used to test the lifetime of catalyst **1** at 80 °C. In fact, catalyst **1** showed living nature within 60 min at 80 °C for ethylene polymerization. As shown in Fig. 6, GPC traces of the polymers produced at different times shifted to the higher molecular weight region with prolonged polymerization time, the number-average molecular weight (M_n) grew linearly with the polymerization time, and the PDI (M_w/M_n) values remained below 1.10. Therefore, catalyst **1** was a living system for ethylene polymerization below 80 °C. To the best of our knowledge, the temperature of 80 °C reached the highest value at which the living polymerization of ethylene was realized to date [59].

Additional ethylene polymerizations at high temperatures were performed at a high ethylene pressure of 6 atm because high pressure could minimize the influence of temperature on the ethylene solubility in the reaction medium (Table 3). At an ethylene pressure of 6 atm, catalyst 1 showed significantly improved catalytic activity and produced the polyethylene with slightly reduced branching density, indicating accelerating chain growing rate and reducing chain walking rate at high polymerization pressures. At 80 °C, catalyst **1** still kept a living manner and produced ultrahigh molecular weight polyethylene ($M_n > 1000 \text{ kg/mol}$) with a narrow polydispersity of 1.10. A further increase in temperature up to 100 °C led to a decrease in activity and molecular weight. High temperature polymerization results at different time periods ranging from 15 to 60 min showed that the turnover frequency (TOF) of catalyst **1** reduced gradually and the molecular weight nonlinearly increased (Fig. 7) with prolonged polymerization time, suggesting a nonliving manner at 100 °C in combination with broad PDI values (PDI = 1.2–1.3). However, catalyst 1 was thermostable and did not decompose on the basis of increased catalytic efficiency, which was calculated gravimetrically on the basis of the weight of the produced polymer and the experimental number-average molecular weight, to the amount of nickel catalyst used [97-99]. In combination with increased PDI values, it was safely concluded that ethylene polymerization with catalyst 1 produced a low molecular weight polymer with broad distribution because the chain transfer



Fig. 6. Plots of M_n (\blacktriangle) and M_w/M_n (PDI) (\blacksquare) as a function of reaction time and GPC traces using 1/Et₂AlCl at 80 °C (conditions: 1.2 atm, 2 µmol Ni, Al/Ni = 600).

Table 3	
Ethylene polymerization results using nickel catalyst 1 at 6 atm. ^{a.}	

Entry	T(°C)	t(min)	Yield (g)	TOF ^b	M _n (kg/mol)	PDI ^c	BD ^d (/1000C)	Catalytic efficiency ^d
1	80	30	1.27	45.4	1106	1.10	94	0.57
2	100	15	0.52	37.1	385	1.15	96	0.68
3	100	30	0.84	30.0	545	1.20	97	0.77
4	100	45	1.16	27.6	599	1.26	97	0.97
5	100	60	1.35	24.1	636	1.28	97	1.06

^a Polymerization conditions: 2 µmol of nickel, Et₂AlCl as cocatalyst, Al/Ni = 600, 6 atm ethylene pressure, 50 mL toluene and 1 mL CH₂Cl₂.

^b TOF in kmol E/(mol Ni·h).

^c M_n and PDI were determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C.

^d Catalytic efficiency was calculated by equation of yield/(2 μ mol \times M_n).



Fig. 7. Plots of TOF and M_n as a function of polymerization time using **1** under 100 °C and 6 atm.

took place at 100 °C. A reduction in the TOF at 100 °C could result from encapsulation of the nickel species into the precipitated high molecular weight polymer [59].

Commonly, conventional α -diimine nickel catalysts with methyl and acenaphthene backbones underwent rapid decompositions above 60 °C because of the acceleration of N-aryl rotation from a perpendicular to a square-planar coordination plane [8,59]. The conformationally locked cyclophane-based nickel catalyst was shown to be thermally stable for the polymerization of ethylene at temperatures up to 70 °C [52]. We previously reported that the steric demand of the dibenzobarrelene backbone could inhibit rotation of the *N*-aryl bonds by the repulsive interaction of the bulky backbone with aniline moieties, thereby enhancing the thermal stability and living fashion of the α -diimine catalyst [59,60]. In this work, the introduction of methoxy groups on the dibenzobarrelene backbone further improved the thermal stability and living fashion of the α -diimine catalyst, which was largely attributed to the intramolecular interactions by O...H hydrogen bonds between methoxy and isopropyl groups of nickel complex 1. These intramolecular interactions were believed to still exist during polymerization process despite of the presence of the alkylaluminum cocatalyst. The existence of these hydrogen bonds in solution had been proved on the basis of ¹H NMR analysis of ligands mentioned above. Further control experiments showed that no reaction of Et₂AlCl with ligand L1 in toluene took place by ¹H NMR analysis, supporting that Et₂AlCl did not disturb these intramolecular interactions. The intramolecular hydrogen bonding interaction inhibited the N-aryl rotation and locked the perpendicular-coordination plane conformation of the α -diimine nickel catalyst at elevated temperatures, thereby keeping steric blocks at the axial sites and suppressing chain transfer. These weak noncovalent interactions in this system were different from reported covalent interactions in the cyclophane-based nickel catalyst [52], which provided viable access to enhancing thermal stability of the catalyst. Unlike previously reported interactions of polymer-ligand, ligand-metal, and ligand-comonomer modes [27,28,64-84], our work also addressed a new ligand-ligand (intra-ligand) hydrogen bonding interaction operating olefin polymerization. Overall, bulky backbone substituents and noncovalent hydrogen bonding interactions are cooperatively responsible for the living polymerization of ethylene at 80 °C, the highest temperature reported to date.

The polyethylenes produced by catalysts 1–5 were highly branched (87-107/1000C) according to ¹H NMR analyses (Fig. S9), which was consistent with previous observations [59]. ¹³C NMR spectroscopies also revealed that all branches were present, and the short methyl branch accounted for the largest proportion (Fig. S10), which was a result of the chain walking process [23]. These branched polyethylenes produced by nickel catalysts 1-5 exhibited very broad melting endotherms with nearly the same profiles (Fig. S11). Therefore, the substituents with either electron-donating or electron-withdrawing effects on the dibenzobarrelene backbone have almost no effect on the microstructure of polyethylenes, and the steric demand of the dibenzobarrelene backbone dominates the chain walking during ethylene polymerization. Also note that the polymer branching density is not sensitive to the polymerization temperature (Table 2), and there is a mild change of polymer branching density within the tested temperature range (20–80 °C) for dibenzobarrelene based α -diimine nickel catalysts 1–5. This different observation to the classic α diimine nickel catalysts is ascribed to enhanced chain walking ability by the bulky dibenzobarrelene backbone [8,59,100].

3. Conclusions

In summary, we have reported dibenzobarrelene-based α diimine nickel catalysts with different electron donating/withdrawing groups (X = OMe, H, Cl, Br, and I) on the ligand backbone for living ethylene polymerizations. The introduction of electronwithdrawing halogens enhanced catalytic activity and polymer molecular weight, while the introduction of electron-donating methoxy groups led to a decrease in catalytic activity and polymer molecular weight. Intensive study on substituent effects of dibenzobarrelene backbone revealed that halogen substituents simultaneously showed steric and electronic effects on ethylene polymerization. Catalyst 5 with diiodo (I) substituent showed the highest activity and produced the highest molecular weight polvethylene. This systematic investigation of the electronic modifications of the α -diimine ligand backbone provided a different understanding of the reported electronic modifications of aniline moieties. The intra-ligand hydrogen bonding interactions (C-H...OMe) were initially observed in the methoxy-substituted dibenzobarrelene α -diimine nickel complex, and the weak noncovalent interactions enhanced the catalyst thermal stability and living fashion of ethylene polymerization at high temperatures up to 80 °C by inhibiting rotation of the *N*-aryl bonds. These intra-ligand hydrogen bonding interactions provided a fundamentally new approach in enhancing catalyst thermostability, complementing previous strategies of weak noncovalent interactions employed in modulating catalytic olefin polymerization.

4. Experimental section

4.1. General procedures

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen with standard vacuum-line, Schlenk, or glovebox techniques. Pressures are absolute values in the whole experimental.

4.2. Materials

2,6-diisopropylanilinewas purchased from Aldrich Chemical and distilled under reduced pressure before use. 1,5-Dihydroxyanthraquinone, 1,5-dichloroanthraquinone, 1,5diaminoanthraquinone, vinylene carbonate, and trifluoroacetic anhydride were purchased from Energy Chemical and used as received. Toluene and hexane were refluxed over Na/K alloy before use, dichloromethane was dried over P₂O₅ and was distilled under nitrogen. Et₂AlCl (1.0 M in hexane) 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.

4.3. Characterization

The NMR data of organic compounds were obtained on a Bruker 400 MHz instrument in CDCl₃ using TMS as a reference at ambient temperature. The ¹³C NMR data of polymers were recorded 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, using 30 ppm for the main chain of PE as a reference. Elemental analyses were performed on a Vario EL macro analyzer. Mass spectra were obtained using electro- spray ionization (ESI) LCMS-2010A for ligands and matrix assisted laser desorption ionization time of flight mass (MALDI-TOF) Bruker ultrafleXtreme for complexes. DSC analyses were conducted with a PerkinElmer DSC-7 system. The DSC curves were recorded as second heating curves from -100 to 150 °C at a heating rate of 10 °C/min and a cooling rate of 10 °C/min. GPC analyses of the molecular weights and molecular weight distributions (PDI = M_w/M_p) of the PE samples at 150 °C were performed on a PL-GPC 220 high-temperature chromatograph equipped with a triple-detection array, including a differential refractive-index detector, a two-angle light-scattering detector, and a four-bridge capillary viscometer. The detection angles of the LS detector were 15 and 90°, and the laser wavelength was 658 nm. 1,2,4-Trichlorobenzene (TCB) was used as the eluent at a flow rate of 1.0 mL/min.

4.4. Crystal structure determination

The crystal was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The X-ray diffraction data was obtained with the ω - 2θ scan mode on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Cu K_{α} radiation (λ = 1.54178 Å) at 150 K. The structure was solved using direct methods, and further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package. All non-

hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in the calculated positions with the displacement factors of the host carbon atoms.

4.5. Ethylene polymerization procedure at atmospheric pressure

In a typical procedure, a round bottom Schlenk flask with stirring bar was heated for 2 h at 150 °C under vacuum and then cooled to ambient temperature. The flask was pressurized to 1.5 atm of ethylene and vented for three times. The appropriate Et₂AlCl compound as cocatalyst and toluene were added into the glass reactor under 1.2 atm of ethylene. The system was continuously stirred for 5 min, and then toluene and 1 mL of a solution of catalyst in CH₂Cl₂ were added sequentially by syringe to the well-stirred solution, and the total reaction volume was kept at 21 mL. The ethylene pressure was kept constant at 1.2 atm by continuous feeding of gaseous ethylene throughout the reaction. The other 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 ethanol/HCl) after continuously stirring for an appropriate period. The resulting precipitated polymers were collected and treated by filtration, washed with methanol for several times, and dried in vacuum at 40 °C to a constant weight.

4.6. Ethylene polymerization procedure at high pressure

A mechanically stirred 100 mL Parr reactor was heated to 150 °C for 2 h under vacuum and then cooled to room temperature. The autoclave was pressurized to 6 atm of ethylene and vented three times. The autoclave was then charged with solution of Et₂AlCl in toluene under 1.2 atm of ethylene at initialization temperature. The system was maintained by continuously stirring for 5 min, and then 1 mL solution of nickel complex in CH₂Cl₂ was charged into the autoclave under 1.2 atm of ethylene. The ethylene pressure was raised to the specified value. 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 a certain time. 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 40 °C to a constant weight.

4.7. Synthesis of α -Diimine compounds

L1, Ar–N=C(An)–(An)C=N–Ar (An = 1,5-dimethoxydibenzobarrelene, Ar = 2,6-diisopropylphenyl). 1,5-Dimethoxyanthracene was prepared by substitution and reduction reaction according to the literature procedure (see SI) [85,86]. The α-dione compound (1,5-dimethoxy-9,10-dihydro-9,10-ethanoan thracene-11,12-dione) was prepared according to a previous method [90]. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.34–7.28 (m, 2H, Ph), 7.09 (s, 1H, Ph), 7.07 (s, 1H, Ph), 6.88 (s, 1H, Ph), 6.86 (s, 1H, Ph), 5.42 (s, 2H, CH), 3.87 (s, 6H, CH₃).



 α -Diimine ligand L1 was synthesized by the reaction of 1,5-di methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dione with 2,6-diisopropylphenylamine in toluene. A typical synthetic procedure for L1 was as follows: 1,5-Dimethoxy-9,10-dihydro-9,10-etha noanthracene-11,12-dione and 2,6-diisopropylphenylamine were charged in a round bottom flak with touluene (50 mL). A catalytic amount of *p*-toluenesulfonic acid was added and the reaction was heated to reflux for 24 h in the atmosshere of nitrogen. The resulting water was removed as an azeotropic mixture using a Dean-Stark apparatus. After the reaction finished, the mixture was cooled to ambient tempetature and the solvent was removed in vaccum. The product was obtained as yellow crystals in 82% yield after rectystallization from hot ethanol. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.24-7.06 (m, 8H, Ph), 6.84-6.76 (d, 2H, Ph), 6.71-6.64 (d, 2H, Ph), 5.36 (s, 2H, CH), 3.68 (s, 6H, CH₃), 2.50 (m, 4H, CH), 1.21-1.13 (d, 6H, CH₃),1.12-1.05 (d, 6H, CH₃), 1.05-0.96 (t, 12H, CH₃). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): 158.32, 154.87, 140.86, 136.62, 136.05, 129.54, 129.21, 128.22, 126.88, 124.59, 123.83, 122.67, 122.51, 119.99, 109.19, 55.15, 44.52, 28.76, 28.38, 23.37, 22.86, 22.33, 22.01. Anal. Calcd for C₄₂H₄₈N₂O₂: C, 82.31; H, 7.89; N, 4.57. Found: C, 82.58; H, 7.95; N, 4.60. ESI-MS (m/z): 613 [M +H]⁺; 635 [M+Na]⁺.



L3, Synthesis of Ar—N=C(An)—(An)C=N—Ar (An = 1,5-dichlorodibenzobarrelene, Ar = 2,6-diisopropylphenyl). 1,5-Dichloroanthracene was prepared according to the reported literature (see SI) [87]. Following the above procedure, the α-dione compound (1,5-di-chloro-9,10-dihydro-9,10-ethanoanthracene-11,12dione) was isolated as orange solids. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.49–7.31 (m, 6H, Ph), 5.50 (s, 2H, CH).



α-Diimine ligand **L3** was obtained as yellow crystals in 90% yield. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.25–7.09 (m, 12H, Ph), 5.40 (s, 2H, CH), 2.45 (m, 4H, CH), 1.30–1.20 (d, 6H, CH₃), 1.77–1.08 (d, 6H, CH₃), 1.07–0.95 (t, 12H, CH₃). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): 156.17, 145.92, 140.26, 136.72, 136.50, 135.23, 131.07, 128.58, 128.30, 124.31, 122.98, 122.54, 48.13, 29.07, 28.52, 23.31, 22.59, 22.01, 21.79. Anal. Calcd for C₄₀H₄₂N₂-Cl₂: C, 77.28; H, 6.81; N, 4.51. Found: C, 77.56; H, 6.99; N, 4.80. ESI-MS (*m*/*z*): 622 [M+H]⁺; 643 [M+Na]⁺.



L4, Synthesis of Ar—N=C(An)—(An)C=N—Ar (An = 1,5-dibromodibenzobarrelene, Ar = 2,6-diisopropylphenyl). 1,5-Dibromoanthracene was prepared according to the reported literature (see SI) [88]. 1,5-Dibromo-9,10-dihydro-9,10-ethanoanthra cene-11,12-dione was isolated as orange solids. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.62 (d, 1H, Ph), 7.60 (d, 1H, Ph), 7.49 (s, 1H, Ph), 7.47 (s, 1H, Ph),7.31–7.25 (m, 2H, Ph), 5.51 (s, 2H, CH).



α-Diimine ligand **L4** was obtained as yellow crystals in 80% yield. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.42–7.33 (d, 2H, Ph), 7.25–7.13 (m, 8H, Ph), 7.10–7.03 (t, 2H, Ph), 5.37 (s, 2H, CH), 2.43 (m, 4H, CH), 1.32–1.22 (d, 6H, CH₃), 1.16–1.08 (d, 6H, CH₃), 1.08–0.95 (dd, 12H, CH₃). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): 140.41, 138.63, 136.59, 135.05, 131.47, 128.79, 124.97, 124.07, 123.18, 122.53, 120.50, 50.84, 29.16, 28.58, 23.31, 22.58, 22.00, 21.88. Anal. Calcd for $C_{40}H_{42}N_2Br_2$: C, 67.61; H, 5.96; N, 3.94. Found: C, 67.89; H, 6.19; N, 3.73. ESI-MS (*m*/*z*): 711 [M+H]⁺; 733.1 [M+Na]⁺.



L5, Synthesis of Ar—N=C(An)–(An)C=N—Ar (An = 1,5-diiododibenzobarrelene, Ar = 2,6-diisopropylphenyl). 1,5-Diiodoanthracene was prepared according to the literature (see SI) [89]. 1,5-Di-iodo-9,10-dihydro-9,10-ethanoanthracene-11,12-d ione was isolated as orange solids. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.86 (d, 1H, Ph), 7.84 (d, 1H, Ph), 7.50 (d, 1H, Ph), 7.48 (d, 1H, Ph), 7.14–7.08 (t, 2H, Ph), 5.37 (s, 2H, CH).



α-Diimine ligand **L5** was obtained as yellow crystals in 85% yield. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.64–7.55 (d, 2H, Ph), 7.25–7.12 (m, 8H, Ph), 6.95–6.86 (t, 2H, Ph), 5.27 (s, 2H, CH), 2.47 (m, 4H, CH), 1.39–1.28 (d, 6H, CH₃), 1.13–1.04 (dd, 12H, CH₃), 1.03–0.96 (d, 6H, CH₃). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): 139.84, 138.80, 138.58, 138.47, 137.73, 137.09, 135.01, 129.96, 129.09, 126.70, 125.87, 125.21, 124.33, 122.47, 95.48, 65.42, 64.23, 55.78, 55.16, 29.20, 28.96, 28.46, 28.25, 24.14, 23.41, 23.01, 22.56, 22.39, 22.23, 21.80. Anal. Calcd for C₄₀H₄₂N₂I₂: C, 59.71; H, 5.26; N, 3.48. Found: C, 59.90; H, 5.57; N, 3.70. ESI-MS (*m/z*): 805.5 [M+H]⁺; 827.5 [M+Na]⁺.



5. Synthesis of α-diimine nickel complexes

5.1. Synthesis of 1

Ligand L1 (612 mg, 1 mmol) and (DME)NiBr₂ (308 mg, 1 mmol) were combined in a Schlenk tube with 20 mL dried dichloromethane, and the reaction mixture was then stirred overnight at ambient temperature. The solution was filtered through Celite, and the solvent of the filtrate was removed in vacuum. The residue was recrystallized from CH_2Cl_2 /hexane to give nickel complex 1 as dark brown powder in 60% yield.

1, $(Ar-M=C(An)-(An)C=M-Ar)NiBr_{2}$ (An = 1,5-dimethoxydibenzobarrelene, Ar = 2,6-diisopropylphenyl): Anal. Calcd for C₄₂-H₄₈Br₂N₂O₂Ni: C, 60.68; H, 5.82; N, 3.37; Found: C, 61.13; H, 6.29; N, 3.51. MALDI-TOF (*m*/*z*): 832.359 [M+H]⁺; 782.558 [M-Br+K]⁺; 613.380 [ligand+H]⁺.

5.2. Synthesis of 3

Following the above described procedure, the reaction of (DME) $NiBr_2$ and L3 gave complex 3 in 65% yield.

3, $(Ar-N=C(An)-(An)C=N-Ar)NiBr_2$ (An = 1,5-dicholodibenzobarrelene, Ar = 2,6-dimethylphenyl): Anal. Calcd for C₄₀-H₄₂Br₂Cl₂N₂Ni: C, 57.18; H, 5.04; N, 3.33; Found: C, 57.62; H,5.49; N, 3.66. MALDI-TOF <math>(m/z): 841.336 [M+H]⁺; 799.378 [M-Br +K]⁺; 622.10 [ligand+H]⁺.

5.3. Synthesis of 4

Following the above described procedure, the reaction of (DME) $NiBr_2$ and L4 gave complex 4 in 67% yield.

4, $(Ar-N=C(An)-(An)C=N-Ar)NiBr_2$ (An = 1,5-dibromodibenzobarrelene, Ar = 2,6-dimethylphenyl): Anal. Calcd for C₄₀-H₄₂Br₄N₂Ni: C, 51.71; H, 4.56; N, 3.02; Found: C, 52.05; H, 4.69; N, 2.81. MALDI-TOF (*m*/*z*): 930.698 [M+H]⁺; 888.268 [M-Br+K]⁺; 711.256 [ligand+H]⁺.

5.4. Synthesis of 5

Following the above described procedure, the reaction of (DME) NiBr₂ and **L5** gave complex **5** in 63% yield.

5, $(Ar-N=C(An)-(An)C=N-Ar)NiBr_2$ (An = 1,5-diiododibenzobarrelene, Ar = 2,6-dimethylphenyl): Anal. Calcd for C₄₀- $H_{42}Br_4I_2N_2Ni: C, 49.96; H, 4.14; N, 2.74; Found: C, 50.42; H, 4.30; N, 2.89. MALDI-TOF ($ *m*/*z*): 1024.991 [M+H]⁺; 984.189 [M-Br+K]⁺; 805.365 [ligand+H]⁺.

Declaration of Competing Interest

The authors declare no competing financial interest.

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Appendix A. Supplementary material

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