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Nickel(II) Complexes with Three-Dimensional Geometry α -Diimine Ligands: Synthesis and Catalytic Activity toward Copolymerization of Norbornene

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Supporting Information

ABSTRACT: A series of three-dimensional geometry 9,10dihydro-9,10-ethanoanthracene-11,12-diimines (L1–L4) and their nickel(II) dibromide complexes (C1–C4) were synthesized and characterized. The nickel complexes C1–C4, with three-dimensional geometry, exhibited very high activities for norbornene (NB) homopolymerization with only $B(C_6F_5)_3$ as cocatalyst,: for C2 even up to 5.53×10^7 g of polymer/((mol of Ni) h). To investigate the activation of polar monomer, complexes C2 and C3 were selected for copolymerization of NB and 5-norbornene-2-yl acetate (NB-OCOMe) in relatively high activities $(1.6-5.8 \times 10^5 \text{ g of polymer/((mol of Ni) h))}$ and high molecular weights $((0.2-2.8) \times 10^5 \text{ g/mol})$ as well as narrow molecular weight distributions (MWD < 2 for all



polymers) depending on the variation of feed ratios. The reactivity ratios of the NB and NB-OCOMe monomers for C2/ B(C_6F_5)₃ system by the Kelen–Tüdös method were determined to be $r_{\text{NB-OCOMe}} = 0.05$ and $r_{\text{NB}} = 6.72$, respectively. Moreover, the mechanism of polymerization catalyzed by the novel three-dimensional geometry nickel(II) complexes was presented and supported by an end group analysis of the polymer and density functional theory (DFT) calculations of the reaction. The substituent effect of the catalysts and the interaction between Ni²⁺ and NB were discussed, and the results showed that α -dimine nickel complexes with greater steric hindrance and smaller HOMO–LUMO gaps could achieve higher reactivity.

INTRODUCTION

Bicyclo[2.2.1]hept-2-ene (norbornene, NB) and its derivatives have three polymerization methods: ring-opening metathesis polymerization (ROMP),^{1–8} cationic or radical polymerization,⁹ and vinyl-type polymerization.^{10–20} Due to the vinyltype polynorbornene (PNB) high glass transition temperature, high optical transparency, low dielectric constant, and low birefringence, it has been the subject of many studies. Meanwhile, incorporation of polar functionalities into the polynorbornene backbone can change their physical properties,^{21–25} such as toughness, adhesion, surface properties (paintability, wettability, and printability), solvent resistance, blend compatibility with other functional polymers, and rheological properties.

Different catalysts can lead to different polymerization methods of norbornene; thus, the design and synthesis of catalysts are very important. It is well-known that the vinyl addition polymerization of norbornene can be efficiently carried out using conventional Ziegler–Natta catalysts,^{26,27} metal-locene catalysts,^{28–30} and late-transition-metal catalysts.^{31,32} Recently, because of the lower oxophilicity and resistance

toward deactivation by polar functionalities, the design of late-transition-metal catalysts has received renewed interest.^{33–44} The common late-transition-metal catalysts are Ni(II) and Pd(II) complexes. Extensive investigations have favored Ni(II) complexes, because of their better catalytic performance and their illustrated reaction mechanisms.⁴⁵

Bulky α -diimine nickel complexes which show high catalytic activity for α -olefin polymerization have been successfully developed by Brookhart and his collaborators.^{46–48} The utilization of α -diimine Ni(II) complexes for norbornene polymerization has attached much interest in both the academic and industrial fields over the past dozen years. The catalytic features rely on the electronic or steric influence of the ligand used; therefore, substantial work has been conducted on substituent variation of the α -diimine ligands.^{49,50} Much of this work has focused on changing the N-bound aryl group^{51–53} or modifying the backbone,⁵⁴ including the use of axial donating diimine ligands.⁵⁵ Considering that a substituted bulky

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Scheme 1. Synthesis Route of α -Diimine Nickel Complexes



backbone may enhance the stability of nickel α -diimine complexes by hindering the rotation of aniline moieties and protecting the metal center effectively, three-dimensional geometry diimine ligands with great hindrance have been selected. Especially, to the best of our knowledge, the research into three-dimensional geometry diimine ligands of nickel catalysts is still rare.

In this study, a series of three-dimensional geometry 9,10dihydro-9,10-ethanoanthracene-11,12-diimine ligands (L1–L4) and their nickel(II) dibromide complexes (C1–C4) were designed and synthesized, and the catalytic activities of complexes C1–C4 with only $B(C_6F_5)_3$ as cocatalyst in NB polymerization were also investigated. All complexes appeared to be highly active catalysts of vinyl NB polymerization; complexes C2 and C3 displayed high activities toward copolymerization of NB and NB-OCOMe. In particular, we had aimed at investigating the reaction mechanisms and the different reactivities of different catalysts by the ¹⁹F NMR analysis of the polymer end group and density functional theory (DFT) calculations of the reaction.

RESULTS AND DISCUSSION

Synthesis of α -Diimine Ligands and of Nickel(II) Complexes. The stoichiometric condensation reaction of 9,10-dihydro-9,10-ethanoanthracene-11,12-dione and various anilines produced α -diimine ligands L1–L4. All α -diimine ligands L1–L4 formed α -diimine nickel(II) dibromide complexes C1–C4 in good yields by reaction with dimethoxyethane nickel dibromide in dichloromethane (Scheme 1). The α -diimine ligands and nickel complexes were characterized by elemental analysis, single-crystal X-ray diffraction analysis, and NMR spectroscopy.

X-ray Crystallographic Studies. Dark red crystals were obtained by slow diffusion of hexane into a dichloromethane solution of complexes C1–C4, whereas yellow single crystals of ligands L1–L4 suitable for X-ray diffraction analysis were obtained by slow diffusion of petroleum ether into their ethyl acetate solutions. The ORTEP plots of all complexes and ligands are shown in Figures 1–4 and Figures S1–S4 (in the Supporting Information). The crystallographic data are



Figure 1. ORTEP plot of C1 showing the atom-labeling scheme. Hydrogen atoms and some carbon atoms are omitted for clarity.



Figure 2. ORTEP plot of C2 showing the atom-labeling scheme. Hydrogen atoms and some carbon atoms are omitted for clarity.

summarized in Tables S1 and S2 (Supporting Information). Tables S3 and S4 (Supporting Information) give the selected



Figure 3. ORTEP plot of C3 showing the atom-labeling scheme. Hydrogen atoms and some carbon atoms are omitted for clarity.



Figure 4. ORTEP plot of C4 showing the atom-labeling scheme. Hydrogen atoms and some carbon atoms are omitted for clarity.

bond lengths and angles of complexes and ligands. In these complexes, the coordination geometries of the complexes C1, C3, and C4 were demonstrated to be very similar in the solid state. They were both mononuclear and four-coordinate. However, the crystal structure of C2 showed a binuclear complex, where each nickel atom is five-coordinate. The two nickel atoms together with two bromine atoms form a planar four-membered ring.

Homopolymerization of NB. First of all, NB polymerization activities of the synthesized complexes were investigated (Scheme 2). In all polymerizations, $B(C_6F_5)_3$ was selected as cocatalyst; it could be seen that C_6F_5 transferred from $B(C_6F_5)_3$ to nickel in norbornene polymerization.^{16,20}

Scheme 2. Homopolymerization of NB Catalyzed by α -Diimine Nickel Complexes



Four Ni(II) complexes were tested as catalysts in the same system with $B(C_6F_5)_3$ as cocatalyst and chlorobenzene as the reaction solvent (Table 1). Polymer yields and catalytic activities depended on the reaction conditions. In order to determine the most suitable homopolymerization conditions, initial investigations of NB homopolymerization catalyzed by $C2/B(C_6F_5)_3$ were conducted under various conditions, such as different temperatures, NB/Ni ratios, and B/Ni ratios. It was found that the conditions at 90 °C with the NB/Ni ratio at

10000/1 and B/Ni ratio at 5/1 is the most effective. All of the complexes demonstrated high activities on the order of $(0.01-5.53) \times 10^7$ g of polymer/((mol of Ni) h) under optimal conditions. Among the complexes, complex C2 had the highest activity, 5.53×10^7 g of polymer/((mol of Ni) h). Especially, it was far higher than the activities of conventional Ni dimines $(10^5 \text{ g of polymer/((mol of Ni) h)})$. 56,57 Large steric substituents on the aryl rings can effectively shield the axial plane of the central metal and suppress the side reaction of chain growth. Furthermore, with an increasing number of electron-donating substituents on the aryl rings. C3 demonstrated higher activity in comparison to C1, while complex C4 with an electron-withdrawing para substituent on the aryl ring exhibited the lowest catalytic activity. The obtained PNBs were completely soluble in chlorobenzene and dichlorobenzene at room temperature, which indicated a low stereoregularity.

Copolymerization of NB and NB-OCOMe. Since the Ni(II)/B(C₆F₅)₃ system had high activity (5.53 × 10⁷ g of polymer/((mol of Ni) h) toward NB homopolymerization, C2 and C3 were selected as catalysts to investigate whether they also had high activities toward copolymerization of NB with NB-OCOMe. A series of copolymerizations of NB with NB-OCOMe were investigated with the catalyst system Ni(II)/B(C₆F₅)₃ in chlorobenzene at 60 °C for 1 h under a nitrogen atmosphere (Scheme 3).

From Table 2, we could also find that the catalytic activity of $C2/B(C_6F_5)_3$ was higher than that of $C3/B(C_6F_5)_3$. However, NB-OCOMe could not be homopolymerized under the same conditions. This was common for functionalized NB derivatives, in which the oxygen atom competes with the double bond for coordination. A high concentration of oxygen atoms would impede double-bond coordination.^{58–60} The copolymers of NB and NB-OCOMe were soluble in common organic solvents (such as CHCl₃, CH₂Cl₂, cyclohexane, THF) as well as chlorobenzene, exhibiting better solubility than PNB.

To obtain the reactivity ratios of NB and NB-OCOMe monomers, we selected $C2/B(C_6F_5)_3$ as the catalytic system and changed the polymerization time and the feed content of catalysts to control the conversion rate to be under 10%. The results are shown in Table S5 (Supporting Information). The reactivity ratios were determined by the Kelen–Tüdös method (Figure 5),⁶¹ which is shown in eqs 1–4. For C2/B(C₆F₅)₃, the reactivity ratio of NB-OCOMe was 0.05 and the reactivity ratio of NB was 6.72.

$$x = \frac{[\text{NB-OCOCH}_3]}{[\text{NB}]} \quad y = \frac{\text{d}[\text{NB-OCOCH}_3]}{\text{d}[\text{NB}]} \tag{1}$$

$$\eta = \left(r_{\text{NB-OCOCH}_3} + \frac{r_{\text{NB}}}{\alpha}\right)\xi - \frac{r_{\text{NB}}}{\alpha} \tag{4}$$

$$F = \frac{x^2}{y} \quad G = \frac{x(y-1)}{y} \quad \alpha = \sqrt{F_{\max} \times F_{\min}}$$
(2)

$$\eta = \frac{G}{\alpha + F} \quad \xi = \frac{F}{\alpha + F} \tag{3}$$

Characterizations of Copolymers. The obtained copolymers were characterized by GPC, and the corresponding data are shown in Table 2. The molecular weights of the obtained

entry	complex	NB/Ni (mol/mol)	B/Ni (mol/mol)	T (°C)	reaction time (min)	PNB yield (%)	$activity^b$
1	C2	5000	20	60	10	48.13	1.36
2	C2	10000	20	60	10	73.64	4.16
3	C2	15000	20	60	10	22.65	1.92
4	C2	20000	20	60	10	6.69	0.75
5	C2	10000	0	60	С	с	С
6	C2	10000	2.5	60	10	41.60	2.35
7	C2	10000	5	60	2	96.48	27.25
8	C2	10000	10	60	2	82.03	23.17
9	C2	10000	20	60	10	73.64	4.16
10	C2	10000	40	60	10	47.97	2.71
11	C2	10000	60	60	10	16.82	0.95
12	C2	10000	5	0	30	4.78	0.09
13	C2	10000	5	30	30	39.30	0.74
14	C2	10000	5	60	2	96.48	27.25
15	C2	10000	5	90	1	97.93	55.30
16	C2	10000	5	120	1	80.30	45.35
17	C1	10000	5	90	1	29.12	16.45
18	C3	10000	5	90	1	33.60	18.98
19	C4	10000	5	90	1	15.29	8.64

^{*a*}Reaction conditions: chlorobenzene, 22 mL; Ni complex, 5×10^{-6} mol. ^{*b*}In units of 10^{6} g of polymer/((mol of Ni) h). ^{*c*}Not determined.

Scheme 3. Copolymerization of NB and NB-OCOMe Catalyzed by α -Diimine Nickel Complexes



copolymers were up to 10^5 , and the molecular weight distributions (MWDs) of the obtained polymers were all relatively narrow (MWD < 2). The molecular weights of copolymers in the C2/B(C₆F₅)₃ system were somewhat higher than those of polymers obtained from C3/B(C₆F₅)₃.

These obtained copolymers were characterized by spectra (FTIR, ¹H NMR) and thermal analysis (DSC, TGA). In Figure S5 (Supporting Information), the signal of the double bond at



Figure 5. Kelen-Tüdös method plot of η versus ξ for NB/NB-OCOMe copolymerization (based on NMR analysis of the copolymers catalyzed by C2/B(C₆F₅)₃ systems).

1710 cm⁻¹, assigned to the C=C bond of the ROMP structure of PNB, was not observed. The signals at about 941 cm⁻¹ could be attributed to the bicyclo[2.2.1]heptane ring. The observation of a signal at 1740 cm⁻¹ in the spectra confirmed that the NB-OCOMe monomer had been inserted into the chains of the copolymers in vinyl-type addition rather than physical

Fable 2. Copolymerization	of NB and NB-OCOMe	Catalyzed by Nickel Con	nplex C2 or C3 Combine	d with $B(C_6F_5)_3^a$
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entry	cat.	NB/NB-OCOMe (mol/mol)	reaction time (min)	yield (%)	$activity^b$	$M_{ m w}^{\ c}$	$M_{\rm w}/M_{\rm n}^{\ c}$	NB-OCOMe (mol %) ^{d}
1	C2	100/0	1	82.03	2.3×10^{7}	е	е	е
2	C2	80/20	60	55.23	5.8×10^{5}	2.8×10^{5}	1.5	7.28
3	C2	60/40	60	34.2	4.0×10^{5}	1.9×10^{4}	1.4	8.23
4	C2	50/50	60	32.6	1.6×10^{5}	1.5×10^{4}	1.4	10.23
5	C2	0/100	60	trace	е	е	е	е
6	C3	100/0	2	90.42	1.6×10^{6}	е	е	е
7	C3	80/20	60	46	4.8×10^{5}	1.0×10^{5}	1.5	6.10
8	C3	60/40	60	25	2.9×10^{5}	1.5×10^{4}	1.5	7.18
9	C3	50/50	60	trace	е	е	е	е

^{*a*}Conditions: $c[\text{cat.}] = 5.0 \times 10^{-6} \text{ mol/L};$ cocatalyst B(C₆F₅)₃, B/complex/monomer (*n/n/n*) 10/1/10000, polymerization temperature 60 °C, solvent chlorobenzene, total volume 22 mL. ^{*b*}In units of g of polymer/((mol of Ni) h). ^{*c*}Determined by GPC vs polystyrene standards in THF. ^{*d*}Determined by ¹H NMR spectroscopy in CDCl₃. ^{*c*}Not determined.

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blends. Figure S6 (Supporting Information) proved that the polymers were vinyl-addition type by the absence of a resonance of the proton hydrogen connected to the double bond at 5.3-5.9 ppm. The peaks at 0.9-1.3 ppm were assigned to the hydrogen corresponding to 5'/6'/6, the peaks at 1.5-1.7ppm were assigned to the hydrogen corresponding to 7'/7, the peaks at 1.9-2.2 ppm were assigned to the hydrogen corresponding to 1'/2'/3'/4'/1/2/3/4/8, and the peaks at 5.0 ppm qwew assigned to the hydrogen corresponding to 5. All the ¹H NMR spectra of the obtained copolymer had two blocks of broadened signals (0.9-2.2 and 4.9-5.0 ppm). Each block corresponded to 1'/2'/3'/4'/5'/6'/7'/1/2/3/4/6/8 and 5. If we assume the NB-OCOMe content as x_i , each block was calculated to contain 10 + x and x protons. The ratio (10 + x)/(10 + x)x corresponds to the integral ratio of these two blocks (A/B). From this equation, x could be calculated as 10B/A - B.

sum of 4.9-5.0 ppm region= B



sum of 0.9-2.2 ppm region= A

The content of NB-OCOMe in copolymers was calculated from 6.1 to 10.2% by varying the comonomer feed ratios (NB-OCOMe/NB) from 10 to 50%.⁶²

The TGA curves of the copolymers with different NB-OCOMe contents prepared by C2/B(C₆F₅)₃ and C3/B(C₆F₅)₃ are shown in Figure S7 (Supporting Information). The decomposition temperatures ($T_{\rm d}$ s) of the polymers were as high as 321.5–408.1 °C and decreased with an increase of the NB-OCOMe content in the copolymers. The DSC curves and glass transition temperatures ($T_{\rm g}$ s) of the copolymers with different NB-OCOMe ratios prepared by Ni(II)/B(C₆F₅)₃ are shown in Figure S8 (Supporting Information). The $T_{\rm g}$ s of the polymers were reduced to 265.9–304.2 °C when the content of NB-OCOMe was increased in the copolymers.

All of the copolymers, irrespective of the polymerization conditions employed, showed identical powder WXRD patterns. Figure S9 (Supporting Information) shows the WXRD curves of the copolymers with different NB-OCOMe contents prepared by $C2/B(C_6F_5)_3$ and $C3/B(C_6F_5)_3$. There was no trace of Bragg reflections in the characteristic crystalline regions; thus, the polymers are noncrystalline. The occurrence of two halos at 2θ values of 9.82-11.14 and $17.86-19.03^{\circ}$ are characteristic for PNB. The packing density became smaller with an increase of NB-OCOMe content in the copolymers, and the packing densities of the copolymers obtained by $C2/B(C_6F_5)_3$ were smaller than those obtained by $C3/B(C_6F_5)_3$.

Mechanism of NB Polymerization. In order to establish the NB polymerization mechanisms catalyzed by Ni catalysts used in the experiments, we analyzed the end group of the polymer and carried out a DFT calculation for the reaction.⁶³ Toward the polymerization initiation step, the most direct proof of an initiation mechanism would come from elucidation of the end group structure of the polymers.^{16,20} The solubilities of the polymers produced in CDCl₃ in Table 1 were too poor

and the polymers were thus not suitable for NMR determination of end groups. The unambiguous characterization of the end groups for copolymers (NB-OCOMe content 7.28%) in Table 2 by $^{19}\mathrm{F}$ NMR spectra enabled us to construct a mechanism of chain initiation and termination.

The ¹⁹F NMR spectrum (Figure 6) of copolymers demonstrated that the resonances observed came from a



Figure 6. ^{19}F NMR spectrum of NB/NB-OCOMe copolymers (NB-OCOMe content 7.28%) obtained with C2/B(C₆F₅)₃.

 C_6F_5 group appended to the polymer, presumably at the end of the polynorbornene chain. The p-fluorine was assigned to the peak at -158.1 ppm (1F). The two *m*-fluorines, which theoretically should also be nonequivalent, were evidently accidentally degenerate and resonate at -162.9 ppm (2F) and apparently were not affected by the stereochemistry of the last polymer chain units.⁶⁴ The two *o*-fluorines should be nonequivalent; one of them was syn to the norbornene bridging methylene, and the other was anti. If the pentafluorophenyl end group experienced hindered rotation around the phenyl ipso carbon-norbornene carbon single bond, separate resonances would be expected for the ofluorines. Indeed, two groups of signals were observed at -133.1 (1F) and -140.1 ppm (1F) and were assigned to the two o-fluorines. The chemical shifts and the number of the absorption peaks were consistent with those reported.¹⁶ It could be concluded that the polymerization initiation mechanism via insertion of the norbornene monomer into the Ni–C bond of the C_6F_5 ligand was supported by the ¹⁹F NMR spectrum of a copolymer containing the resonances of C₆F₅.

In Figure 7, in the first step, the NB molecule coordinates perpendicularly to the complex R1 to form the π complex IN1. For IN1, the two NB carbon atoms are located 2.113 and 2.205 Å from the nickel atom. The coordination of NB to complex R1 leads to a decrease in energy to 27.61 kcal mol⁻¹, which indicates that this process is exothermic. The formation of a new carbon-metal bond (complex IN1) is complete at this stage. The rate-determining step of the chain propagation is NB insertion from complex NB to PR1 through transition state 1 (TS1) (Figure S10, Supporting Information). The NB molecule in complex IN1, which is also perpendicular to the plane of the metal coordination sphere, rotates into the equatorial plane and forms two new bonds from the two carbon atoms originally bonded to the metal. Simultaneously, the alkyl group on the catalyst migrates from the metal to one of the C



Figure 7. Proposed mechanism and energy profile of NB polymerization catalyzed by Ni catalyst.

atoms of NB through TS1 to produce the product PR1. This complexation assists the insertion of NB into the metal–carbon bond via a four-membered cyclic transition state. For this process, the energy barrier is about 19.93 kcal mol⁻¹. At the TS1 point, the distance between C_1 and C_2 lengthens from 1.391 Å in IN1 to 1.492 Å in TS1. After TS1, the complex PR1 formed, which possesses an energy of 3.22 kcal mol⁻¹ above IN1. The product of insertion (PR1) resembles the structure of IN1 in that a new vacant coordination site is available for the next NB to coordinate and propagate the chain. The coordination of NB to PR1 results in a decrease in energy of about 14.37 kcal mol⁻¹ to produce the complex R2.

In order to understand the effect of the catalyst structure variation on the Ni catalysis activity, the substituent effect of the catalyst and the interaction between Ni²⁺ and NB will be discussed in detail. The orbital interaction diagram is given in Figure S11 (Supporting Information). According to these orbital models, the interactions between the ligand (NB) and Ni²⁺ in IN1 comprise mainly two components. Therefore, the two NB-metal bonding orbitals are occupied in IN1. First, the interactions of the occupied π orbital of the ligand (NB) with the $d_{x^2-y^2}$ orbital of Ni²⁺ result in σ and σ^* orbitals. In fact, the HOMO-1 orbital represents the orbital interaction of the p orbital of the ligand (NB) with the $d_{x^2-y^2}$ orbital of the Ni atom. At the same time, the π^* orbital of NB and d_{xy} orbital of Ni²⁺ also overlap to produce the π and π^* orbitals between NB and Ni²⁺ (Figure S11). The HOMO orbital represents the interaction of the π^* orbital of NB and the d_{xy} orbitals of Ni²⁺. In fact, the interaction of the π^* orbital of NB and d_{xy} orbitals of Ni²⁺ result in a lengthening of the C=C bond of NB, which leads to activation of the carbon-carbon double bond (Figure S12, Supporting Information). Thus, the HOMO is very important for the activation of NB in that there are strong π interactions between NB and Ni²⁺.

The relevant frontier molecular orbitals (FMOs) of Ni catalyst and NB in this reaction are presented in Figure S13 (Supporting Information). It is easy to find that the energy difference between HOMO_{Ni} (HOMO of Ni catalyst) and LUMO_{NB} (LUMO of NB) is greater than that of HOMO_{NB} (HOMO of NB) and LUMO_{Ni} (LUMO of Ni catalyst); therefore, the main HOMO–LUMO interaction occurs

between $LUMO_{Ni}$ and $HOMO_{NB}$ and the charges are transferred from NB to Ni catalyst in the reaction process. All these results indicate that a smaller HOMO–LUMO gap was more reactive. From Figure 8, the HOMO–LUMO gaps



Figure 8. Relevant FMOs of NB and different Ni catalysts in this reaction.

predicted for the reactions of NB with four different Ni catalysts are 0.205, 0.210, 0.211, and 0.216 au for C2, C3, C1, and C4, respectively. Thus, the complex C2 has a better catalyzing activity than the other three kinds of Ni catalysts, which is consistent with the experimental results.

CONCLUSIONS

A series of new three-dimensional geometry α -diimine nickel complexes were synthesized and characterized by single-crystal X-ray techniques. Despite the fact that there have been many reported α -diimine systems in the literature, the threedimensional geometry α -diimine ligands show superior steric hindrance on the nickel center and herein represent a new polymerization mechanism for α -diimine catalytic systems. Toward NB polymerization, these new three-dimensional geometry α -diimine nickel complexes showed high activities, for C2 even up to 5.53×10^7 g of polymer/((mol of Ni) h), which was the highest activity for NB polymerization over α diimine nickel catalysts in the current report. α -Diimine nickel complexes with greater steric hindrance and a smaller HOMO-LUMO gap could achieve even higher reactivity. The polymerization initiation mechanism via insertion of the norbornene monomer into the Ni-C bond of the C₆F₅ ligand was supported by the ¹⁹F NMR analysis of the polymer end

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group and DFT calculations of the reaction. These findings identify a promising strategy to explore high-reactivity catalysts by designing three-dimensional geometry α -diimine catalytic systems with large steric hindrance.

EXPERIMENTAL SECTION

General Considerations. All the reactions were performed under an atmosphere of dry and oxygen-free argon using standard vacuum and Schlenk techniques or under a nitrogen atmosphere in a glovebox (MBraun). Chlorobenzene was refluxed and distilled from sodium under dry nitrogen; dichloromethane was dried over CaH2. NB was purchased from Alfa Aesar, purified through drying by sodium and distilled under dry nitrogen, and then dissolved in chlorobenzene. 5-Norbornen-2-yl acetate was purchased from Aldrich and purified by anhydrous magnesium sulfate. Other commercially available reagents were purchased and used without purification. The intensity data of the single crystals were collected on a CCD-Bruker Smart APEX II system. Elemental analysis was performed on an Elementar-Vario EL cube elemental analyzer. The nuclear magnetic resonance (NMR) spectra of the polymers were recorded on a Bruker ARX 400 NMR spectrometer at ambient temperature, with CDCl₃ as the solvent. Chemical shifts for the ¹H and ¹³C NMR spectra are given in parts per million from the peak for internal trimethylsilane. The ¹⁹F NMR spectra are referenced to external CFCl₃. An XT4A melting point instrument (BeiJing KeYi electro-optic instrument factory, China) was used to test the melting point temperature. Gel permeation chromatography (GPC) was conducted with a Breeze Waters system using polystyrene as the standard and tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min. The FTIR spectra were recorded with a Shimadzu IR Prestige-21 FTIR spectrophotometer. Wide-angle X-ray diffraction (WXRD) curves were recorded on a Bruker D8 Focus Xray diffractometer, operating at 40 kV and 40 mA with a copper target $(\lambda = 1.54 \text{ Å})$ and a scanning rate of 2°/min. The thermal gravimetric analysis (TGA) measurements were performed on a Perkin-Elmer TGA 7 instrument from room temperature to 700 °C at a rate of 10 °C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were obtained on a Shimadzu DSC-60 instruemtn with a heating/cooling rate of 10 °C/min under a nitrogen atmosphere.

Synthesis of α -Diimine Ligands L1–L4. The α -diimine ligands L1–L4 were synthesized by the reaction of 9,10-dihydro-9,10-ethanoanthracene-11,12-dione⁶⁵ with the corresponding aniline in toluene. A typical synthetic procedure for L1 is as follows: under a nitrogen atmosphere, to a solution of 30 mmol of 2,6-dimethylaniline in 150 mL of toluene were added 10 mmol of 9,10-dihydro-9,10ethanoanthracene-11,12-dione and a catalytic amount of p-toluenesulfonic acid. The mixture was heated under reflux. The resulting water was removed as an azeotropic mixture using a Dean-Stark apparatus. After 24 h, the reaction mixture was cooled to room temperature and evaporated at reduced pressure. The residual solids were further purified by silica column chromatography (20/1 v/v petroleum ether/ ethyl acetate) and were crystallized from a mixture of petroleum ether and ethyl acetate to give the ligand L1 as yellow crystals in 96.1% yield. Ligand L1 was characterized by elemental analysis, single-crystal X-ray diffraction analysis, and ¹H and ¹³C NMR spectroscopy. Mp: 213-214 °C. Anal. Found: C, 87.31; H, 6.40; N, 6.29. Calcd: C, 87.24; H, 6.41; N, 6.36. ¹H NMR (CDCl₃, δ , ppm): 1.88 (s, 12H), 4.86 (s, 2H), 7.04-7.25 (m, 14H). ¹³C NMR (CDCl₃, δ, ppm): 17.81, 51.13, 123.51, 125.61, 126.08, 127.71, 128.39, 138.05, 147.90, 159.64.

Ligand L2 was obtained as yellow crystals in 95.2% yield. Mp: 196– 197 °C. Anal. Found: C, 86.94; H, 7.94; N, 5.12. Calcd: C, 86.91; H, 8.02; N, 5.07. ¹H NMR (CDCl₃, δ , ppm): 1.02 (d, 12 H, *J* = 6.8 Hz), 1.15 (d, 12 H, *J* = 6.8 Hz), 2.49 (m, 4 H), 4.978 (s, 2 H), 7.05–7.25 (m, 14H). ¹³C NMR (CDCl₃, δ , ppm): 22.49, 23.29, 51.10, 122.79, 124.12, 125.40, 127.27, 136.38, 138.57, 145.56, 158.44.

Ligand L3 was obtained as yellow crystals in 87.2% yield. Mp: 227–228 °C. Anal. Found: C, 87.23; H, 6.91; N, 5.86. Calcd: C, 87.14; H, 6.88; N, 5.98. ¹H NMR (CDCl₃, δ , ppm): 1.84 (s, 12 H), 2.36 (s, 6 H), 4.89 (s, 2 H), 7.23 (s, 4H), 7.21 (m, 8H). ¹³C NMR (CDCl₃, δ ,

ppm): 17.78, 20.90, 51.05, 125.20, 125.43, 127.60, 128.42, 132.59, 138.22, 145.40, 159.89.

Ligand L4 was obtained as yellow crystals in 75.6% yield. Mp: 194– 195 °C. Anal. Found: C, 64.21; H, 4.41; N, 4.65. Calcd: C, 64.23; H, 4.38; N, 4.68. ¹H NMR (CDCl₃, δ , ppm): 1.84 (s, 12 H), 4.85 (s, 2 H), 7.20–7.25 (m, 8H), 7.28 (s, 4H). ¹³C NMR (CDCl₃, δ , ppm): 17.68, 51.09, 116.33, 125.28, 127.88, 128.02, 130.51, 137.64, 146.82, 160.32.

Synthesis of α -Diimine Nickel Dibromide Complexes C1– C4. The α -diimine nickel dibromide complexes C1–C4 were synthesized by the reaction of dimethoxyethane nickel dibromide with the corresponding aniline in dichloromethane. A typical synthetic procedure for C1 is as follows: 0.2 mmol of ligand L1 and 0.2 mmol of dimethoxymethane nickel dibromide were added in a Schlenk tube together with 10 mL of dried dichloromethane. The reaction mixture was then stirred for 8 h at room temperature, and 10 mL of absolute hexane was added. The dark red complex crystallized from a mixture of dichloromethane and hexane in 85% yield. Complex C1 was characterized by elemental analysis, single-crystal X-ray diffraction analysis, and ¹H NMR spectroscopy. Mp: 343–344 °C. Anal. Found: C, 58.34; H, 4.26; N, 4.24. Calcd: C, 58.32; H, 4.28; N, 4.25. ¹H NMR (CDCl₃, δ , ppm): 1.92 (s, 12 H), 5.05 (s, 2 H), 7.03–7.52 (m, 14H).

Complex C2 was obtained as dark red crystals in 89% yield. Mp: 320–321 °C. Anal. Found: C, 62.26; H, 5.76; N, 3.62. Calcd: C, 62.29; H, 5.75; N, 3.63. ¹H NMR (CDCl₃, δ , ppm): 1.03 (d, 12 H, *J* = 6.8 Hz), 1.16 (d, 12 H, *J* = 6.8 Hz), 2.50 (m, 4 H), 5.02 (s, 2 H), 7.11–7.27 (m, 14H).

Complex C3 was obtained as dark red crystals in 80% yield. Mp: 351-352 °C. Anal. Found: C, 59.45; H, 4.65; N, 4.09. Calcd: C, 59.43; H, 4.69; N, 4.08. ¹H NMR (CDCl₃, δ , ppm): 1.86 (s, 12 H), 2.39 (s, 6 H), 5.06 (s, 2 H), 7.24 (s, 4H), 7.33-7.37 (m, 8H).

Complex C4 was obtained as dark red crystals in 88% yield. Mp: 362-364 °C. Anal. Found: C, 47.03; H, 3.25; N, 3.45. Calcd: C, 47.05; H, 3.21; N, 3.43. ¹H NMR (CDCl₃, δ , ppm): 1.85 (s, 12 H), 4.85 (s, 2 H), 7.27–7.52 (m, 8H), 7.96 (s, 4H).

Procedure for Homopolymerization of NB. In a typical procedure, the appropriate $B(C_6F_5)_3$ solid was introduced into a round-bottom glass flask, a certain amount of a chlorobenzene solution of NB (0.5 g/mL) and quantitative nickel complex solution were syringed into the well-stirred solution in order, and the reaction mixture was continuously stirred for an designated period at the polymerization temperature. Polymerizations were terminated by addition of 50 mL of acidified ethanol (10/1 v/v ethanol/HCl). The precipitate of polynorbornene was filtered off, washed with ethanol (3 × 10 mL), and dried under vacuum at 40 °C to a constant weight.

Procedure for Copolymerization of NB and NB-OCOMe. In a typical procedure, the appropriate $B(C_6F_5)_3$ solid was introduced into a round-bottom glass flask, a certain amount of a chlorobenzene solution of NB (0.5 g/mL), the corresponding amount of NB-OCOMe, and quantitative nickel complex solution were syringed into the well-stirred solution in order, and the reaction mixture was continuously stirred for an designated period at 60 °C. Polymerizations were terminated by addition of 50 mL of the acidified ethanol (10/1 v/v ethanol/HCl). The precipitate of polynorbornene was filtered off, washed with ethanol (3 × 10 mL), and dried under vacuum at 40 °C to a constant weight.

Calculation Details. The geometries were optimized by DFT, specifically with the Becke three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation function (B3LYP).^{66,67} All theoretical calculations were performed using the Gaussian 09 suite of programs.⁶³ All structures were optimized by employing the hybrid density functional B3LYP method^{66,67} and the 6-31G(d,p) basis set.⁶⁸ A vibrational frequency calculation was then performed at the optimized geometry belonging to each reactant, product, transition state, and intermediate. We confirmed that all reactants and intermediates had no imaginary frequencies and each transition state had one, and only one, imaginary frequency. The zero-point energies (ZPE) were calculated using the vibrational frequencies. Intrinsic reaction coordinate (IRC) calculations, at the same level of theory,

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were performed to ensure that the transition states led to the expected reactants and products.

ASSOCIATED CONTENT

S Supporting Information

CIF files, tables, and figures giving crystallographic data and additional characterization data for α -diimine ligands L1–L4) and α -diimine nickel(II) dibromide complexes C1–C4 and details of the calculations. 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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