Macromolecules

Enhancing Thermal Stability and Living Fashion in α -Diimine–Nickel-Catalyzed (Co)polymerization of Ethylene and Polar Monomer by Increasing the Steric Bulk of Ligand Backbone

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Supporting Information

ABSTRACT: Development of thermally stable nickel-based catalysts is highly desirable for industrial gas-phase olefin polymerizations. On the basis of the strategy of promoting the thermostability of nickel catalyst by the ligand backbone, we herein reported novel dibenzobarrelene-derived α -diimine nickel precatalysts for ethylene polymerization. Increasing the steric bulk on the ligand backbone was expected to inhibit the *N*-aryl rotation of the α -diimine ligands by the repulsive interactions, thus enhancing thermal stability (100 °C) and living fashion a temperatures up to 80 °C. Bulk ligand backbone also improved tolerance of nickel catalyst toward polar groups, and the α -diimine nickel catalyst containing a 2,6-^tBu-dibenzobarrelene backbone catalyzed living copolymerization of ethylene and methyl 10-undecenoate.



INTRODUCTION

Late transition metal catalysis has played a substantial role in the field of catalytic olefin polymerizations over the years. The famous "nickel effect", that a combination of trace impurities of nickel salts with alkylaluminum compounds catalyzed ethylene dimerization, led directly to the discovery of Ziegler catalysts and is also regarded as a forerunner of today's polyolefin industry.^{1,2} In the early stage, late transition metal catalysts are usually regarded as ethylene oligomerization catalysts and yield dimers or oligomers because of the propensity of alkyl metal complexes for the chain transfer by β -hydride elimination.^{3,4} A prominent example is the industrial Shell higher olefin process (SHOP) developed by Keim, producing linear α -olefins by nickel-catalyzed ethylene oligomerization.⁵

A significant breakthrough in late transition metal catalysts for olefin polymerization is the evolution of α -diimine nickel and palladium catalysts by Brookhart, afforded high-molecularweight polymers.^{6–12} A key feature for producing high molecular weight products lies in suppression of chain transfer (associative displacement or chain transfer to bound monomer) by the steric bulk of the *o*-aryl substituents.^{13–18} Despite high catalytic activity, α -diimine-derived catalysts generally show significant decay of activity and afford reducing molecular weight polymers at elevated temperatures.^{19,20} Conventional α diimine nickel and palladium catalysts undergo rapid decompositions above 60 and 25 °C, respectively.^{19,20} This observation has been attributed to increasing *N*-aryl rotations from perpendicular to square-planar coordination plane at elevated temperatures. It not only decreases steric blocks at the axial sites thus accelerating chain transfer reaction, but also leads to the potential decomposition arising from the C–H activation of the metal center to the ligand. 20

An effective approach to access thermally stable α -diimine derived catalysts is the increasing of the steric bulk on the *o*-aryl substituents as described by Brookhart's mechanistic model, especially rigid aryl instead of alkyl group.²¹⁻³² For instance, the α -diimine nickel catalyst with cyclophane-derived N-aryl substituents developed by Guan has demonstrated remarkable activity for ethylene polymerization at 90 °C (Figure 1A).^{28,2} α -Diimine nickel and palladium catalysts bearing dibenzhydryl (CH(Ph)₂) groups reported by Long, Sun, and Chen are thermally stable at 90 and 80 °C, respectively (Figure 1B). $^{25-27,30-32}$ Despite these contributions, living polymerization of ethylene has not been achieved by α -diimine nickel and palladium catalysts above room temperatures.^{28–32} This is attributed to an occurrence of chain transfer at elevated temperatures although the rotation of N-aryl bonds slows down and the C-H activation cannot occur because of the abstraction of alkyl groups.

Besides, low oxophilicity of nickel catalysts allows for copolymerizing ethylene and polar monomers for the preparation of functional polyolefins with improved properties. Although copolymerizations of ethylene and polar monomers have been successfully accomplished using nickel catalysts, their copolymerization activities are significantly reduced or even suppressed.^{33–35} It should be also noted that most examples

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Figure 1. Thermally stable α -diimine derived metal complexes.

often suffer from low molecular weight of the polymer formed $(M_{\rm n} < 10 \text{ kg/mol})$.⁵ These can be ascribed to poison effect of polar groups on nickel metal center. Living catalyzed-copolymerization of ethylene and polar monomers is an inaccessible goal up to date.^{36–42} Design and development of novel thermostable late transition metal catalysts for living (co)polymerization of ethylene and polar monomers thus remains a great challenge, which is unsurpassed in precise molecular weight attainable as well as microstructure control and is highly desirable for industrial gas-phase olefin polymerizations.^{43–48}

Previously, we provided an alternative approach by increasing the steric bulk of the α -diimine ligand backbone for enhancing the thermal stability of nickel-based catalysts.⁴⁹⁻⁵¹ Coates groups recently reported a α -diimine nickel catalyst with a bulky dibenzobarrelene backbone and the steric hindrance of the dibenzobarrelene substituent was predicted to force the aryl groups closer to the nickel metal center, a feature linked to living character (Figure 1C).⁵² Herein, we have synthesized highly thermostable α -diimine nickel catalysts featuring the more bulky dibenzobarrelene backbone for living polymerization of ethylene at elevated temperatures although nickel and palladium analogues have been synthesized and used to catalytic norbornene polymerization.^{53,54} We envisioned that the bulk of the rigid dibenzobarrelene backbone expectedly inhibited the N-aryl rotation of the α -diimine ligand because of the repulsive interaction,⁵² thus enhancing thermal stability and achieving living fashion at elevated temperatures (Figure 1D). The nickel catalyst 3 containing a bulky 2,6-^tBu-dibenzobarrelene backbone was thermally stable at temperatures as high as 100 °C and catalyzed the living ethylene polymerization at temperatures up 80 °C and living copolymerization of ethylene and methyl 10-undecenoate. To the best of our knowledge, this is the most thermally stable living system for ethylene polymerizations.

RESULTS AND DISCUSSION

Substituted 9,10-dihydro-9,10-ethanoanthracene-11,12-dione compounds were prepared by Diels–Alder addition of commercially available anthracene with vinylene carbonate, hydrolysis, and Swern oxidation reactions.^{55,56} Condensation reactions of α -dione compounds with various anilines facilely produced α -diimine ligands L1–L4 in high yields.^{52–54} Nickel complexes 1–4 with different substituents (Scheme 1) were obtained by addition of the corresponding ligands to a stirring suspension of (dimethoxyethane)NiBr₂ in CH₂Cl₂.

Single crystals of nickel complexes 3 and 4 suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into the nickel complex solution in CH_2Cl_2 . The two nickel complexes display a distorted tetrahedral geometry (Figure 2 and 3). The observed bond lengths and angles are typical for α -

Scheme 1. . Synthesis of α -Diimine Nickel Complexes





Figure 2. Crystal structure of α -diimine nickel complex 3 with thermal ellipsoids of 30% probability (front and side views). The hydrogen atoms are omitted for clarity.



Figure 3. Crystal structure of α -diimine nickel complex 4 with thermal ellipsoids of 30% probability (front and side views). The hydrogen atoms and two CH₂Cl₂ molecules are omitted for clarity.

diimine nickel complexes. It is noteworthy that twist angles of the bulky nickel complexes 3 between the aryl ring plane and the Ni-diimine ring plane are far less than 90° (dihedral angle of 76.6 and 81.5°), suggesting that the aryl rings are twisted away from a perpendicular orientation with respect to the Nidiimine ring plane. These twist angles are also smaller than those of α -diimine nickel complexes with acenaphthene (92.5 and 91.5°), dimethyl (89.2°), and dibenzobarrelene backbone (87.0° for 1).^{53,57} This can be attributed to the repulsive interaction of bulky 2,6-^tBu-dibenzobarrelene backbone with isopropyl substituents on aryl rings, which is anticipated to

Table 1	. Eth	ylene	Poly	merization	Results	Using	Nickel	Catal	ysts	1-4/AlEt,Cl	a
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entry	Ni	T (°C)	yield (g)	act. ^b	$M_{\rm n}~({\rm kg/mol})$	PDI ^c	BD^d	$T_{\rm m}^{e}$ (°C)
1	1	20	0.182	182	110	1.20	84	4.9
2	1	35	0.248	248	136	1.16	87	-4.2
3	1	50	0.281	281	156	1.09	93	-13.7
4	1	65	0.261	261	131	1.07	97	-18.8
5	1	80	trace	_	-	_	_	_
6	2	-20	0.352	704	310	1.89	13	129.4
7	2	0	1.348	2696	96.9	2.14	33	115.9
8	2	20	1.194	2388	41.7	1.96	67	98.1
9	2	35	1.097	2194	33.3	1.42	62	67.7
10	2	50	trace	-	-	-	-	_
11	3	20	0.255	255	132	1.10	78	15.8
12	3	35	0.295	295	161	1.06	79	8.6
13	3	50	0.326	326	157	1.06	82	1.3
14	3	65	0.360	360	139	1.06	83	-9.7
15	3	80	0.185	185	115	1.10	92	-17.9
16	4	0	1.314	2628	237	1.80	25	118.8
17	4	20	1.386	2772	47.9	1.81	51	102.3
18	4	35	0.943	1886	35.5	1.73	53	77.9
19	4	50	0.650	1300	21.3	1.63	69	47.7
20	4	65	0.312	624	12.5	1.49	85	-13.6
21	4	80	trace	_	_	_	_	_

^{*a*}Polymerization conditions: 2 μ mol of nickel, Al(AlEt₂Cl)/Ni = 600, 3 psig of ethylene pressure, 30 min for catalysts 1 and 3, 15 min for catalysts 2 and 4, 20 mL of toluene, and 1 mL of 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 using a light scattering detector. ^{*d*}Branching density, branches per 1000 carbon atoms determined by ¹ H NMR spectroscopy. ^{*e*}Determined by differential scanning calorimetry (DSC), second heating, peak value in broad melting endotherms.



Figure 4. Plots of TOF and molecular weight (M_n) versus reaction time in ethylene polymerization using 3 under 100 °C and 75 psig of ethylene pressure (conditions: 2 μ mol of Ni, Al(AlEt₂Cl)/Ni = 600).

suppress the *N*-aryl rotation at elevated temperatures. Additionally, the rigid dibenzobarrelene backbone effectively shields the back space of nickel center and *tert*-butyl groups show axial steric effect, which significantly slow down chain transfer reactions by associative displacement or chain transfer to bound monomer for ethylene polymerization.¹⁸

Ethylene polymerizations were carried out using nickel complexes 1-4 after activation with Et₂AlCl under various temperatures (Table 1). Comparisons of polymerization results using catalyst 1 vs 2 and 3 vs 4 at the same reaction temperatures clearly demonstrated steric effects of *o*-aryl substituents on ethylene polymerization. As previously reported, increasing the steric bulk of *o*-aryl substituents by substituting the *o*-methyl groups with the *o*-isopropyl groups led to a remarkable increase in polymer molecular weight, thermal stability of catalyst, and branching density.^{19,36} More notably, the molecular weight distribution significantly became narrow. Encouraged by these results, we further investigated backbone substituent effect on ethylene polymerizations using nickel catalysts containing the bulky *o*-isopropyl groups.

As initially envisioned, the introduction of the bulky backbone remarkably enhanced the thermal stability of the α -diimine nickel catalysts. Under ethylene pressure of 3 psig, catalyst 1 displayed the highest activity at 50 °C and afforded the high-molecular-weight polyethylene with a narrow poly-dispersity index (PDI) (entry 3). When the reaction temperature was increased from 50 to 65 °C, the polymerization activity and the molecular weight decreased only by 7% and by 16%, respectively, and PDI still remained narrow (PDI < 1.10). This observation strongly suggested that catalyst 1 was highly thermostable, and no decomposition of nickel species and chain transfer events occurred during ethylene polymerization below 65 °C. The slight reduction of the polymerization activity could be attributed to a decrease in ethylene solubility in toluene with increased temperatures from 50 to 65 °C.

Introducing *tert*-butyl on dibenzobarrelene backbone further improved the thermal stability of nickel catalyst. Catalyst 3 showed the highest activity at 65 °C, and the narrowly dispersed polyethylene (PDI = 1.10) was produced at temperatures up to 80 °C (Figure S5). When the temperature

was increased to 100 °C, catalyst 3 still showed an apparent activity at atmospheric pressure and small amount of polymers was obtained because of extremely low ethylene solubility in toluene at 100 °C. To reliably calculate polymerization yield and probe the thermal stability of catalyst 3, ethylene polymerizations using catalyst 3 were performed under high pressure of 75 psig and 100 °C. The turnover frequencies (TOFs) of catalyst 3 at different time periods ranging from 15 to 60 min were used to test the catalyst lifetime. Figure 4 clearly showed that TOF values remained relatively constant within 30 min whereas molecular weight increased with prolonged polymerization time. A slight reduction in the TOF at 45 min could result from encapsulation of nickel species into the precipitated high-molecular-weight polymer from reaction media. Strikingly, all of the obtained polymers still had PDIs of around 1.40 even at 100 °C. Therefore, the molecular weight, PDI, and TOF data strongly supported that catalyst 3 was remarkably stable at 100 °C.

The living feature of ethylene polymerization was further investigated using 1 at 65 °C and using 3 at 80 °C. Figure 5



Figure 5. Plots of M_n (\blacktriangle) and M_w/M_n (PDI) (\blacksquare) as a function of polymerization time and GPC traces using $1/\text{Et}_2\text{AlCl}$ at 65 °C and 3/ Et₂AlCl at 80 °C (conditions: 3 psig, 2 μ mol Ni, and Al/Ni = 600).

shows symmetric GPC traces of the polymers obtained at different polymerization times without tail peaks, which shift to the higher molecular weight region with the prolonged polymerization time. Plots of number-average molecular weights (M_n) as a function of polymerization time also illustrate that M_n grows linearly with the polymerization time, and PDI (M_w/M_n) values are below 1.16. To the best of our knowledge, the living polymerization of ethylene at temperature

of 80 $^{\circ}\mathrm{C}$ presented here achieves the highest value in the field of catalytic polymerization.

In contrast to the previous work on α -diimine nickel catalysts by substituting dibenzhydryl (CH(Ph)₂) moieties,^{30,31} catalyst 3 showed improved thermal stability and polymerization activity. More importantly, living polymerization of ethylene was also achieved at the highest temperature of 80 °C reported to data, which represented an improvement over other reported nickel-catalyzed olefin polymerization.^{43–48} This behavior can be attributed to the unique nature of the bulky backbone. The steric demand of the dibenzobarrelene backbone not only is expected to inhibit the rotation of *N*-aryl bonds by the repulsive interaction of the bulky backbone with aniline moieties but also shield the back space of nickel center, thereby preventing the catalyst decomposition by the C–H activation and suppressing chain transfer.

The polyethylenes produced by dibenzobarrelene derived α diimine nickel catalysts were branched (Figure S6-S9 in Supporting Information). In particular, nickel catalysts 1 and 3 bearing isopropyl groups afforded highly branched polyethylenes (78-97/1000C) with very broad and ill-defined melting endotherms (Figure S10 and S12 in Supporting Information) in a range of temperatures from 20 to 80 °C. ¹³C NMR spectroscopy also revealed that the resultant PEs mostly contained methyl branches and long branches and the branch-on-branch structure generated through tertiary carbons, specifically a sec-butyl branch (19.40 and 11.37 ppm), was also formed (Figure S6 and S8 in Supporting Information). This observation was stark contrast to the previously reported dibenzobarrelene derived α -diimine nickel system with 2-(2,4,6-trimethylphenyl)ethyl groups (Figure 1C), which produced linear PEs with sharp melting transitions.⁵² Therefore, the dibenzobarrelene derived α -diimine nickel catalyst is a promising candidate for tuning the branching structure of PE by design of the *o*-substituent on the aryl ring.

Methyl 10-undecenoate (MU) was chosen as a comonomer and copolymerizations of ethylene and MU were conducted using catalysts 1 and 3. Copolymerization results in Table 2 demonstrated that the copolymers produced by catalyst 3 with *tert*-butyl groups on dibenzobarrelene backbone showed higher molecular weight and narrower PDI although 3 was less active than 1 for copolymerization of ethylene and MU (entries 1, 2, 3 vs 4, 5, 6). With increased methyl 10-undecenoate concentration, copolymerization activity and molecular weight

Table 2. C	opolymerization	of Ethylene	and Methyl 1	0-Undecenoate U	sing α -Diimine	Nickel Catal	ysts 1 and 3/AlE	t,Cl'
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entry	Ni	T (°C)	[MU] (M)	.yield (mg)	ir. ^b (mol %)	$M_{\rm n}^{\ c} \ ({\rm kg/mol})$	PDI ^c	BD^d
1	1	20	0.05	427	0.41	122	1.10	88
2	1	20	0.1	396	0.76	102	1.15	86
3	1	20	0.2	264	1.29	88	1.23	84
4	3	20	0.05	337	0.42	132	1.04	86
5	3	20	0.1	300	0.77	107	1.07	83
6	3	20	0.2	251	1.32	95	1.09	82
7	3	35	0.1	285	1.00	91	1.14	88
8	3	50	0.1	162	1.40	53	1.40	89
9 ^e	3	20	0.1	278	0.75	88	1.23	81
10	5 ^f	20	0.1	370	2.30	16	2.06	65

^{*a*}Polymerization conditions: 5 μ mol of nickel, Al(AlEt₂Cl)/Ni = 1600, 30 min, 3 psig of ethylene pressure, 20 mL of toluene, and 1 mL of CH₂Cl₂. ^{*b*}Comonomer incorporation, determined by ¹ H NMR spectroscopy. ^{*c*}M_n and PDI were determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C using a light scattering detector. ^{*d*}Branching density, branches per 1000 carbon atoms determined by ¹ H NMR spectroscopy. ^{*e*}Al(AlEt₂Cl)/Ni = 600. ^{*f*}S is a conventional α -diimine nickel complex with acenaphthene backbone. decreased while the incorporation of comonomer increased (entries 4, 5, and 6). Increasing reaction temperature from 20 to 50 °C for catalyst 3 results in an increasing incorporation of comonomer up to 1.40 mol %, however, copolymerization yield and copolymer molecular weight decreased and PDI became broad (entries 6, 7, and 8 in Table 2). When Al/Ni ratio decreased from 1600 to 600 (entry 5 vs 9), the copolymerization yield decreased slightly and PDI became broad. For comparison, a conventional α -diimine nickel catalyst 5 bearing the acenaphthene backbone showed 2.30 mol % incorporation for the copolymerization of ethylene and MU, but the polymer produced by 3 showed much higher molecular weight (107 vs 16 kg/mol) and narrower distribution (1.07 vs 2.06) under same conditions. When MU was added into ethylene polymerization system, polymerization activity and polymer molecular weight decreased more slightly for catalyst 3 relative to 1 with acenaphthene backbone.49

Narrowly dispersed copolymers (PDI < 1.10) were produced by catalyst 3 below 20 °C and 0.2 M MU concentration, suggesting living fashion. The living features of copolymerization were further investigated using catalyst 3 at different reaction times. With prolonged polymerization time, M_n of copolymers grows linearly and M_w/M_n (PDI) values are below 1.10 (Table S7). Moreover, the incorporation of methyl 10undecenoate remained constant (0.77 mol %) (Figure 6). This



Figure 6. Plots of M_n (\blacktriangle), M_w/M_n (PDI), (\blacksquare) and incorporation of MU as a function of polymerization time and using 3/Et₂AlCl at 20 °C and 0.1 M MU (conditions: 3 psig, 5 µmol of Ni, Al/Ni = 1600).

result strongly suggests that comonomer methyl 10-undecenoate is uniformly incorporated into polyethylene chain. Catalyst **3** represents the first nickel based catalyst that can catalyze living copolymerization of ethylene and polar monomers up to date, which is contrast to general knowledge that polar monomers are a typical poison to the transition metal catalysts. In comparison with the previously reported dibenzobarrelene derived α -diimine nickel system with 2-(2,4,6-trimethylphenyl)ethyl groups (Figure 1C), nickel catalysts presented here showed living characteristics and afforded the higher molecular-weight polymer with higher branching degree.⁵²

CONCLUSIONS

In summary, we have reported thermally stable α -diimine nickel catalysts with the bulky dibenzobarrelene backbone that catalyze ethylene polymerization at elevated temperatures. Catalyst 3 containing the 2,6-^tBu-dibenzobarrelene backbone was highly thermostable at 100 °C, and TOFs of ethylene polymerization remained nearly unchanged while the molecular weight increased with prolonged polymerization time. Living polymerizations of ethylene were successfully achieved by catalyst 1 below 65 °C or catalyst 3 below 80 °C. In addition to previously reported access by increasing the steric bulk of the *o*-

aryl substituents, an alternative approach is provided for enhancing the thermal stability of α -diimine nickel catalysts by increasing the steric bulk of the ligand backbone. The enhanced thermal stability of catalyst 3, as well as its ability to achieve living polymerization of ethylene at 80 °C, represents an improvement over other reported catalytic systems. Bulky dibenzobarrelene backbone also improved tolerance of nickel catalyst toward polar groups, and living copolymerizations of ethylene with methyl 10-undecenoate were also achieved by bulky catalyst 3. Future work is focused on catalyst optimization of variations in dibenzobarrelene frameworks and copolymerizations of ethylene with various polar monomers.

EXPERIMENTAL SECTION

All manipulations involving air- and moisture sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard vacuum-line, Schlenk, or glovebox techniques.

Materials. Dichloromethane was distilled from CaH_2 under nitrogen, and toluene and hexane from Na/K alloy. Anthracene, vinylene carbonate, *tert*-butanol, and trifluoroacetic acid were purchased from Energy Chemical and used as received. 2,6-Dimethylaniline and 2,6-diisopropylaniline were purchased from Aldrich Chemical and were distilled under reduced pressure before use. AlEt₂Cl (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. A conventional α -diimine nickel complex 5 bearing the acenaphthene backbone was synthesized according to the literature.¹⁹

Ethylene Polymerization at Atmosphere Pressure. A roundbottom Schlenk flask with stirring bar was heated for 3 h at 150 °C under vacuum and then cooled to room temperature. The flask was pressurized to 15 psig of ethylene and vented three times. The appropriate alkyl aluminum compound as cocatalyst and toluene were added into the glass reactor under 3 psig of ethylene. The system was continuously stirred for 5 min, and then toluene and 1 mL of a solution of nickel complex 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 3 psig 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 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 40 °C to a constant weight.

Ethylene Polymerization 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 75 psig of ethylene and vented three times. The autoclave was then charged with solution of Et₂AlCl in toluene under 3 psig of ethylene at initialization temperature. The system was maintained by continuously stirring for 5 min, and then a 1 mL solution of nickel complex in CH₂Cl₂ was charged into the autoclave under 3 psig 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.

Copolymerization of Ethylene and Methyl 10-Undecenoate (MU). 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 flask was pressurized to 3 psig of ethylene and vented three times.

Then the glass reactor was charged with the required amount of freshly distilled toluene, Et_2AlCl and methyl 10-undecenoate in sequence under 3 psig of ethylene. The system was continuously stirred for 5 min at the desired temperature, and then 1 mL of a solution of nickel complex in CH_2Cl_2 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 3 psig 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. After polymerization process, the reaction was carefully quenched with 10 mL mixture of 10% HCl solution of methanol. The resulting precipitated polymers were collected and treated by filtration, washed with methanol several times, and dried in vacuum at 40 °C to a constant weight.

Measurements. Elemental analyses were performed on a Vario EL microanalyzer. Mass spectra were obtained using electro spray ionization (ESI) LCMS-2010A for ligands. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF) were performed on Bruker ultrafleXtreme for nickel complexes. NMR spectra of organic compounds were carried out on a Bruker 400 MHz instrument in CDCl₃ using TMS as a reference. ¹³C NMR spectra of polymers were carried out on a Bruker 500 MHz at 120 °C. Sample solutions of the polymer were prepared in o-C₆H₄Cl₂/o-C₆D₄Cl₂ (50% v/v) in a 10 mm sample tube. The spectra of the quantitative ¹³C NMR were taken with a 74° flip angle, an acquisition time of 1.5 s, and a delay of 4.0 s. The chemical shifts were referenced to main chain of PE $(-(CH_2)_n-)$ (30 ppm). 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 analysis of the molecular weights and molecular weight distributions (PDI = M_w/M_p) of the polymers at 150 °C were performed on a PL-GPC 220 hightemperature chromatograph equipped with a triple-detection array, including a differential refractive-index detector, a two-angle lightscattering detector, and a four-bridge capillary viscometer. 1,2,4-Trichlorobenzene (TCB) was used as the eluent at a flow rate of 1.0 mL/min.

Crystal Structure Determination. The crystals were mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. Data obtained with the ω -2 θ scan mode was collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Cu K_{α} radiation (λ = 1.54178 Å) at 150 K. The structures were solved using direct methods, while further refinement with full-matrix leastsquares on F^2 was obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Synthesis of α -Diimine Compounds. α -Diimine ligands L1 and L2 were synthesized according to the literature.^{56,57} L1 and L2 were fully confirmed by ¹H and ¹³C NMR.

L1, Ar–N=C(An)–(An)C=N–Ar (An = dibenzobarrelene, Ar = 2,6-diisopropylphenyl). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.25–7.05 (m, 14H, Ph), 4.978 (s, 2H, CH), 2.49 (m, 4H, CH), 1.15 (d, 12H, CH₃), 1.02 (d, 12H, CH₃). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): 158.45, 145.56, 138.57, 136.38, 127.27, 125.40, 124.12, 122.79, 51.10, 23.29, 22.49. Anal. Calcd for C₄₀H₄₄N₂: C, 86.91; H, 8.02; N, 5.07. Found: C, 86.95; H, 7.93; N, 5.12.



L2, Ar–N=C(An)–(An)C=N–Ar (An = dibenzobarrelene, Ar = 2,6-dimethylphenyl). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.25–7.04 (m, 14H, Ph), 4.86 (s, 2H, CH), 1.88 (s, 12H, CH₃). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): 159.64, 147.90, 138.05, 128.39, 127.71,

126.08, 125.61, 123.51, 51.13, 17.81. Anal. Calcd for $C_{32}H_{28}N_2\colon$ C, 87.24; H, 6.41; N, 6.36. Found: C, 87.31; H, 6.40; N, 6.29.



The α -dione compound (2,6-di-*tert*-butyl-9,10-dihydro-9,10-ethanoanthracene-11,12-dione) was prepared according to a previous method and characterized.⁵⁸ ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.46–7.41 (s, 2H, Ph), 7.40–7.35 (s, 4H, Ph), 4.93 (s, 2H, CH), 1.30 (s, 18H, CH₃).



 α -Diimine ligands L3 and L4 were synthesized by the reaction of 2,6-di-tertbutyl-9,10-dihydro-9,10-ethanoanthracene-11,12-dione with the corresponding aniline in toluene. A typical synthetic procedure for L3 is as follows: 2,6-di-*tert*-butyl- 9,10-dihydro-9,10-ethanoanthracene-11,12-dione (1.0 g, 2.88 mmol) and 2,6-diisopropylaniline (1.07 g, 6.06 mmol) were charged in a round-bottom flak with toluene (50 mL). A catalytic amount of *p*-toluenesulfonic acid was added and the reaction heated to reflux under a nitrogen atmosphere. 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 the solvent was removed in vacuum. The residual solids were further purified by recrystallization from ethanol to give L3 as yellow crystals in 90% yield.

L3, Ar–N=C(An)–(An)C=N–Ar (An = 2,6-¹Bu-dibenzobarrelene, Ar = 2,6- diisopropylphenyl). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.25–7.07 (m, 12H, Ph), 4.91 (s, 2H, CH), 2.53 (m, 4H, CH), 1.23 (s, 18H, CH₃), 1.19 (d, 6H, CH₃), 1.12 (d, 6H, CH₃), 1.04 (d, 6H, CH₃), 1.01 (d, 6H, CH₃). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): 158.76, 150.29, 145.61, 138.46, 136.67, 136.33, 135.53, 124.93, 124.11, 123.98, 122.77, 122.68, 122.45, 50.87, 34.79, 31.37, 28.36, 28.20, 23.22, 22.30. ESI-MS (m/z): 665.5 [M + H]⁺; 687.5 [M + Na]⁺. Anal. Calcd for C₄₈H₆₀N₂: C, 86.69; H, 9.09; N, 4.21; Found: C, 86.75; H, 9.11; N, 4.11.



L4 was obtained as yellow crystals in 93% yield. L4, Ar–N= C(An)–(An)C=N–Ar (An = 2,6-^tBu-dibenzobarrelene, Ar = 2,6dimethylphenyl). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.23–6.98 (m, 12H, Ph), 4.79 (s, 2H, CH), 1.91 (s, 6H, CH₃), 1.83 (s, 6H, CH₃), 1.26 (s, 18H, CH₃). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): 160.21, 150.91, 148.05, 137.90, 134.89, 127.70, 125.73, 124.73, 124.25, 123.30, 122.56, 50.93, 31.35, 17.96, 17.60. ESI-MS (m/z): 553.5 [M + H]⁺; 575.5 [M + Na]⁺. Anal. Calcd for C₄₀H₄₄N₂: C, 86.91; H, 8.02; N, 5.07; Found: C, 86.95; H, 7.98; N, 5.03.



Synthesis of α -Diimine Nickel Complexes. α -Diimine nickel complexes 1 and 2 were synthesized according to the previously reported procedures and confirmed by elemental analysis.^{55,54}

1, $(Ar-N=C(An)-(An)C=N-Ar)NiBr_2$ (An = dibenzobarrelene, Ar = 2,6-diisopropylphenyl). Anal. Calcd for C₄₀H₄₄Br₂N₂Ni: C, 62.29; H, 5.75; N, 3.63; Found: C, 62.26; H, 5.76; N, 3.62.

2, $(Ar-N=C(An)-(An)C=N-Ar)NiBr_2$ (An = dibenzobarrelene, Ar = 2,6-dimethylphenyl). Anal. Calcd for $C_{32}H_{28}Br_2N_2Ni$: C, 58.32; H, 4.28; N, 4.25; Found: C, 58.34; H, 4.26; N, 4.24.

Synthesis of **3**. Ligand L3 (665 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 for 6 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 CH₂Cl₂ /hexane to give nickel complex **3** as dark brown powder in 50% yield. **3**, (Ar–N=C(An)–(An)C=N–Ar)NiBr₂ (An = 2,6-^tBu-dibenzobarrelene, Ar = 2,6-diisopropylphenyl): MALDI–TOF (m/z): 884.991 [M + H]⁺; 842.865 [M – Br + K]⁺; 665.796 [ligand + H]⁺. Anal. Calcd for C₄₈H₆₀Br₂N₂Ni: C, 66.25; H, 6.85; N, 3.17; Found: C, 66.28; H, 7.03; N, 2.95.

Synthesis of **4**. Following the above-described procedure, the reaction of (DME)NiBr₂ and L4 give complex **4** in 80% yield. **4** (Ar–N=C(An)–(An)C=N–Ar)NiBr₂ (An = 2,6-^tBu-dibenzobarrelene, Ar = 2,6-dimethylphenyl): MALDI–TOF (m/z): 773.067 [M + H]⁺; 730.936 [M – Br + K]⁺; 553.82 [ligand + H] ⁺. Anal. Calcd for C₄₀H₄₄Br₂N₂Ni: C, 62.29; H, 5.75; N, 3.63; Found: C, 62.05; H, 5.99; N, 3.40.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.7b00121.

Synthesis route, NMR spectra of ligands, ¹H and ¹³C NMR of polymers and assignments, crystallographic data, results of olefin polymerization, DSC curves of polymers, and GPC traces (PDF) Cif file for 3 (CIF)

Cif file for 4 (CIF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. Das mülheimer normaldruck-polyäthylen-verfahren. *Angew. Chem.* **1955**, *67*, 541.

(2) Mecking, S. Olefin polymerization by late transition metal complexes-a root of Ziegler catalysts gains new ground. *Angew. Chem., Int. Ed.* **2001**, *40*, 534.

(3) Peuckert, M.; Keim, W. A new nickel complex for the oligomerization of ethylene. *Organometallics* **1983**, *2*, 594.

(4) Wilke, G. Contributions to organo-nickel chemistry. Angew. Chem., Int. Ed. Engl. 1988, 27, 185.

(5) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. Novel coordination of (benzoylmethylene) triphenylphosphorane in a nickel oligomerization catalyst. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466.

(6) Johnson, L. K.; Killian, C. M.; Brookhart, M. New Pd (II)-and Ni (II)-based catalysts for polymerization of ethylene and. alpha.-olefins. *J. Am. Chem. Soc.* **1995**, *117*, 6414.

(7) Johnson, L. K.; Mecking, S.; Brookhart, M. Copolymerization of ethylene and propylene with functionalized vinyl monomers by palladium (II) catalysts. *J. Am. Chem. Soc.* **1996**, *118*, 267.

(8) Ittel, S. D.; Johnson, L. K.; Brookhart, M. Late-metal catalysts for ethylene homo-and copolymerization. *Chem. Rev.* **2000**, *100*, 1169.

(9) Coates, G. W.; Hustad, P. D.; Reinartz, S. Catalysts for the living insertion polymerization of alkenes: access to new polyolefin architectures using Ziegler-Natta chemistry. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236.

(10) Chen, E. Y. X.; Marks, T. J. Cocatalysts for metal-catalyzed olefin polymerization: activators, activation processes, and structureactivity relationships. *Chem. Rev.* **2000**, *100*, 1391.

(11) Wang, S.; Redshaw, C.; Sun, W.-H. Recent progress on nickelbased systems for ethylene oligo-/polymerization catalysis. *J. Organomet. Chem.* **2014**, 751, 717.

(12) Chen, C.; Luo, S.; Jordan, R. F. Cationic polymerization and insertion chemistry in the reactions of vinyl ethers with (α -diimine) PdMe⁺ species. J. Am. Chem. Soc. **2010**, 132, 5273.

(13) Gottfried, A. C.; Brookhart, M. Living polymerization of ethylene using Pd (II) α -diimine catalysts. *Macromolecules* **2001**, *34*, 1140.

(14) Gottfried, A. C.; Brookhart, M. Living and block copolymerization of ethylene and α -olefins using palladium (II)- α -diimine catalysts. *Macromolecules* **2003**, *36*, 3085.

(15) Ye, Z.; Xu, L.; Dong, Z.; Xiang, P. Designing polyethylenes of complex chain architectures via Pd-diimine-catalyzed "living" ethylene polymerization. *Chem. Commun.* **2013**, *49*, 6235.

(16) Guan, Z. Control of polymer topology by chain-walking catalysts. *Chem. - Eur. J.* **2002**, *8*, 3086.

(17) Gao, H.; Hu, H.; Zhu, F.; Wu, Q. A thermally robust amineimine nickel catalyst precursor for living polymerization of ethylene above room temperature. *Chem. Commun.* **2012**, *48*, 3312.

(18) Deng, L.; Woo, T. K.; Cavallo, L.; Margl, P. M.; Ziegler, T. The role of bulky substituents in Brookhart-type Ni (II) diimine catalyzed olefin polymerization: a combined density functional theory and molecular mechanics study. J. Am. Chem. Soc. **1997**, 119, 6177.

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

(20) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. Mechanistic studies of Pd (II)- α -diimine-catalyzed olefin polymerizations. J. Am. Chem. Soc. **2000**, 122, 6686.

(21) Schmid, M.; Eberhardt, R.; Klinga, M.; Leskelä, M.; Rieger, B. New $C_{2\nu}$ -and chiral C_2 -symmetric olefin polymerization catalysts based on nickel (II) and palladium (II) diimine complexes bearing 2,6diphenyl aniline moieties: synthesis, structural characterization, and first insight into polymerization properties. *Organometallics* **2001**, *20*, 2321.

(22) Meinhard, D.; Wegner, M.; Kipiani, G.; Hearley, A.; Reuter, P.; Fischer, S.; Marti, O.; Rieger, B. New nickel (II) diimine complexes and the control of polyethylene microstructure by catalyst design. *J. Am. Chem. Soc.* **2007**, *129*, 9182.

(23) Ionkin, A. S.; Marshall, W. ortho-5-Methylfuran-and benzofuran-substituted η^3 -allyl (α -diimine) nickel (II) complexes: syntheses, structural characterization, and the first polymerization results. *Organometallics* **2004**, *23*, 3276. (24) Allen, K. E.; Campos, J.; Daugulis, O.; Brookhart, M. Living polymerization of ethylene and copolymerization of ethylene/methyl acrylate using "sandwich" diimine palladium catalysts. *ACS Catal.* **2015**, *5*, 456.

(25) Liu, H.; Zhao, W.; Hao, X.; Redshaw, C.; Huang, W.; Sun, W.-H. 2,6-Dibenzhydryl-N-(2-phenyliminoacenaphthylenylidene)-4methylbenzenamine nickel dibromides: synthesis, characterization, and ethylene polymerization. *Organometallics* **2011**, *30*, 2418.

(26) Zhou, Z.; Hao, X.; Redshaw, C.; Chen, L.; Sun, W. Nickel bis {4,6-dibenzhydryl-2-[(arylimino) methyl] phenoxylate} complexes: synthesis, structures, and catalytic behaviour towards ethylene and norbornene. *Catal. Sci. Technol.* **2012**, *2*, 1340.

(27) Du, S.; Kong, S.; Shi, Q.; Mao, J.; Guo, C.; Yi, J.; Liang, T.; Sun, W. Enhancing the activity and thermal stability of nickel complex precatalysts using 1-[2,6-bis (bis (4-fluorophenyl) methyl)-4-methyl phenylimino]-2- aryliminoacenaphthylene derivatives. *Organometallics* **2015**, *34*, 582.

(28) Camacho, D. H.; Salo, E. V.; Ziller, J. W.; Guan, Z. Cyclophanebased highly active late-transition-metal catalysts for ethylene polymerization. *Angew. Chem., Int. Ed.* **2004**, *43*, 1821.

(29) Camacho, D. H.; Guan, Z. Living polymerization of α -olefins at elevated temperatures catalyzed by a highly active and robust cyclophane-based nickel catalyst. *Macromolecules* **2005**, *38*, 2544.

(30) Rhinehart, J. L.; Brown, L. A.; Long, B. K. A robust Ni (II) α diimine catalyst for high temperature ethylene polymerization. *J. Am. Chem. Soc.* **2013**, 135, 16316.

(31) Rhinehart, J. L.; Mitchell, N. E.; Long, B. K. Enhancing α -diimine catalysts for high-temperature ethylene polymerization. *ACS Catal.* **2014**, *4*, 2501.

(32) Dai, S.; Sui, X.; Chen, C. Highly robust palladium (II) α -diimine catalysts for slow-chain-walking polymerization of ethylene and copolymerization with methyl acrylate. *Angew. Chem., Int. Ed.* **2015**, *54*, 9948 Other nickel and palladium catalysts can polymerize ethylene at elevated temperatures, but living characteristics cannot be achieved..

(33) Berkefeld, A.; Mecking, S. Coordination copolymerization of polar vinyl monomers H_2C =CHX. *Angew. Chem., Int. Ed.* **2008**, 47, 2538.

(34) Boardman, B. M.; Bazan, G. C. α-Iminocarboxamidato nickel complexes. Acc. Chem. Res. 2009, 42, 1597.

(35) Mu, H.; Pan, L.; Song, D.; Li, Y. Neutral nickel catalysts for olefin homo-and copolymerization: relationships between catalyst structures and catalytic properties. *Chem. Rev.* **2015**, *115*, 12091.

(36) Schneider, Y.; Azoulay, J. D.; Coffin, R. C.; Bazan, G. C. New polyethylene macroinitiators and their subsequent grafting by atom transfer radical polymerization. *J. Am. Chem. Soc.* **2008**, *130*, 10464.

(37) Zhao, Y.; Gao, H.; Liang, G.; Zhu, F.; Wu, Q. Synthesis of welldefined amphiphilic branched polyethylene-graft-poly (N-isopropylacrylamide) copolymers by coordination copolymerization in tandem with RAFT polymerization and their self-assembled vesicles. *Polym. Chem.* **2014**, *5*, 962.

(38) Dai, S.; Zhou, S.; Zhang, W.; Chen, C. Systematic investigations of ligand steric effects on α -diimine palladium catalyzed olefin polymerization and copolymerization. *Macromolecules* **2016**, *49*, 8855–8862.

(39) Guo, L.; Dai, S.; Sui, X.; Chen, C. Palladium and nickel catalyzed chain walking olefin polymerization and copolymerization. *ACS Catal.* **2016**, *6*, 428.

(40) Chen, M.; Chen, C. Rational design of high-performance phosphine sulfonate nickel catalysts for ethylene polymerization and copolymerization with polar monomers. *ACS Catal.* **2017**, *7*, 1308.

(41) Chen, M.; Yang, B.; Chen, C. Redox-controlled olefin (co)polymerization catalyzed by ferrocene-bridged phosphine-sulfonate palladium complexes. *Angew. Chem., Int. Ed.* **2015**, *54*, 15520.

(42) Dai, S.; Chen, C. Direct synthesis of functionalized highmolecular-weight polyethylene by copolymerization of ethylene with polar monomers. *Angew. Chem., Int. Ed.* **2016**, *55*, 13281.

(43) Hu, H.; Zhang, L.; Gao, H.; Zhu, F.; Wu, Q. Design of thermally stable amine-imine nickel catalyst precursors for living polymerization of ethylene: effect of ligand substituents on catalytic behavior and polymer properties. *Chem. - Eur. J.* 2014, 20, 3225.

(44) Hu, H.; Gao, H.; Chen, D.; Li, G.; Tan, Y.; Liang, G.; Zhu, F.; Wu, Q. Ligand directed regioselectivity in amine-imine nickelcatalyzed 1-hexene polymerization. *ACS Catal.* **2015**, *5*, 122.

(45) Zai, S.; Liu, F.; Gao, H.; Li, C.; Zhou, G.; Guo, L.; Zhang, L.; Zhu, F.; Wu, Q.; et al. Longstanding living polymerization of ethylene: substituent effect on bridging carbon of 2-pyridinemethanamine nickel catalysts. *Chem. Commun.* **2010**, *46*, 4321.

(46) Zai, S.; Gao, H.; Huang, Z.; Hu, H.; Wu, H.; Wu, Q. Substituent effects of pyridine-amine nickel catalyst precursors on ethylene polymerization. *ACS Catal.* **2012**, *2*, 433.

(47) Cherian, A. E.; Rose, J. M.; Lobkovsky, E. B.; Coates, G. W. A C_2 -symmetric, living α -diimine Ni (II) catalyst: regioblock copolymers from propylene. *J. Am. Chem. Soc.* **2005**, *127*, 13770.

(48) Xu, Y.; Xiang, P.; Ye, Z.; Wang, W. Hyperbranched-linear polyethylene block polymers constructed with chain blocks of hybrid chain topologies via one-pot stagewise chain walking ethylene "living" polymerization. *Macromolecules* **2010**, *43*, 8026.

(49) Liu, F.; Hu, H.; Xu, Y.; Guo, L.; Zai, S.; Song, K.; Gao, H.; Zhang, L.; Zhu, F.; Wu, Q. Thermostable α -diimine nickel (II) catalyst for ethylene polymerization: effects of the substituted backbone structure on catalytic properties and branching structure of polyethylene. *Macromolecules* **2009**, *42*, 7789.

(50) Guo, L.; Gao, H.; Guan, Q.; Hu, H.; Deng, J.; Liu, J.; Liu, F.; Wu, Q. Substituent effects of the backbone in α -diimine palladium catalysts on homo-and copolymerization of ethylene with methyl acrylate. *Organometallics* **2012**, *31*, 6054.

(51) Liu, J.; Chen, D.; Wu, H.; Xiao, Z.; Gao, H.; Zhu, F.; Wu, Q. Polymerization of α -olefins using a camphyl α -diimine nickel catalyst at elevated temperature. *Macromolecules* **2014**, 47, 3325.

(52) Long, B. K.; Eagan, J. M.; Mulzer, M.; Coates, G. W. Semicrystalline polar polyethylene: ester-functionalized linear polyolefins enabled by a functional-group-tolerant, cationic nickel catalyst. *Angew. Chem., Int. Ed.* **2016**, *55*, 7106.

(53) Huo, P.; Liu, W.; He, X.; Wang, H.; Chen, Y. Nickel (II) complexes with three-dimensional geometry α -diimine ligands: synthesis and catalytic activity toward copolymerization of norbornene. *Organometallics* **2013**, *32*, 2291.

(54) Huo, P.; Liu, W.; He, X.; Wei, Z.; Chen, Y. Substituent effects and activation mechanism of norbornene polymerization catalyzed by three-dimensional geometry α -diimine palladium complexes. *Polym. Chem.* **2014**, *5*, 1210.

(55) Mondal, R.; Shah, B. K.; Neckers, D. C. Photogeneration of heptacene in a polymer matrix. J. Am. Chem. Soc. 2006, 128, 9612.

(56) Amon, C. M.; Banwell, M. G.; Gravatt, G. L. Oxidation of vicinal diols to α -dicarbonyl compounds by trifluoroacetic anhydride-activated dimethyl sulfoxide. *J. Org. Chem.* **1987**, *52*, 4851.

(57) Gomes, C. S.; Gomes, P. T.; Duarte, M. T. α -Diimine transitionmetal complexes: Mechanochemistry-a new synthetic approach. *J. Organomet. Chem.* **2014**, 760, 101.

(58) Bredenkötter, B.; Grzywa, M.; Alaghemandi, M.; Schmid, R.; Herrebout, W.; Bultinck, P.; Volkmer, D. Tribenzotriquinacene receptors for C_{60} fullerene rotors: Towards C_3 symmetrical chiral stators for unidirectionally operating nanoratchets. *Chem. - Eur. J.* **2014**, 20, 9100.