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2,6-Dibenzhydryl-*N*-(2-phenyliminoacenaphthylenylidene)-4-methylbenzenamine Nickel Dibromides: Synthesis, Characterization, and Ethylene Polymerization

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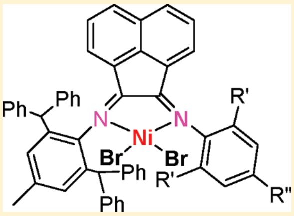
S *Supporting Information*

ABSTRACT: A series of 2,6-dibenzhydryl-*N*-(2-phenyliminoacenaphthylenylidene)-4-methylbenzenamines (**L1**−**L5**) and the nickel(II) dibromide complexes thereof (**C1**−**C5**) were synthesized and fully characterized. The molecular structures of representative complexes were determined by single-crystal X-ray diffraction and revealed a distorted-pyramidal geometry at nickel. All nickel(II) procatalysts exhibited very high activity for the polymerization of ethylene, with activities as high as the range of 10^7 g of PE (mol of Ni)$^{-1}$ h^{-1}.



1. INTRODUCTION

In comparison with early-metal-based systems, late-transition-metal catalysts have some unique features[1] which have led to great interest in this field in the last few decades. In particular, following the observations by Brookhart and co-workers,[2] the number of research papers in this area has mushroomed.[3] We have been attracted by the use of N^N^N tridentate procatalysts and have designed a number of new ligands, namely 2-imino-1,10-phenanthrolines,[4] 2-(2- benzimidazolyl)-1,10-phenanthrolines,[5] 2-(benzoxazolyl)-1,10-phenanthrolines,[6] 2-(2-benzimidazolyl)-6-(1-(arylimino)ethyl) pyridines,[7] 2-(benzoxazolyl)-6-(1-(arylimino)ethyl)pyridines,[8] and 2-quinoxalinyl-6-iminopyridines.[9] The metal complexes with these ligands exhibited favorable catalytic activity for either the selective oligomerization or polymerization of ethylene. At the same time, we have also reported N^N bidentate procatalysts utilizing ligands such as 2-(2-pyridyl) quinoxaline,[10] 2-ethylcarboxylate-6-iminopyridine,[11] and pyrazolyliminophosphorane.[12]

In general, late-transition-metal olefin oligo-/polymerization catalysts tend to utilize one of the metals iron, cobalt, nickel, and palladium.[13] Both iron(II)- and nickel(II)-based systems have been shown to be very adaptable in terms of their ability to afford a variety of products.[14] This has been achieved by simple tuning of the ancillary ligand set, which allows the product compositions to vary from that of small oligomers to high molecular weight polyethylene with narrow molecular weight distribution. In the case of α-diimines, either the ligand backbone or the substituents associated with the N-bound aryl can readily be manipulated to suit the required electronic and/or steric features.[1] As a result, a variety of ligand sets for polymerization catalysts have been designed in recent years.[15] Indeed, even now, driven by the thirst for new polyethylene materials with high molecular weight and extraordinary properties, researchers continue to develop new ligand systems with the potential to induce high catalytic activity, new product properties, or better still both of these features.

Although substantial work has been conducted on substituent variation for the diimine ligand set, with much of the focus on changing the N-bound aryl group[16] or modifying the backbone,[16,17] including the use of axial donating diimine ligands,[18] unsymmetrical diimine ligands still remain rare.[19] Previous studies have shown that the phenyl ring orientation places the bulky substituents in axial sites, which effectively retards the rate of chain transfer relative to chain propagation.[20] The present goal is to synthesize a new bulky aniline which when incorporated into the α-diimine system will prohibit free rotation about the aryl−nitrogen bonds and thereby induce novel catalytic features for the resulting metal procatalysts. Such a feature has been employed to good effect in Guan's cyclophane-based nickel complexes[21] and our recent unsymmetrical bis(imino)pyridyliron procatalysts.[22] Herein, the synthesis, characterization, and catalytic behavior of the 2,6-dibenzhydryl-*N*-(2-phenyliminoacenaphthylenylidene)-4-methylbenzenamine nickel complexes (**C1**−**C5**) are reported. These new bulky unsymmetrical α-diimine nickel procatalysts are capable of ethylene polymerization with high activity up to a value of 10^7 g of PE (mol of Ni)$^{-1}$ h^{-1}. Interestingly, the polymer produced with different cocatalysts (Et_2AlCl or MAO) possessed quite diverse microstructures.

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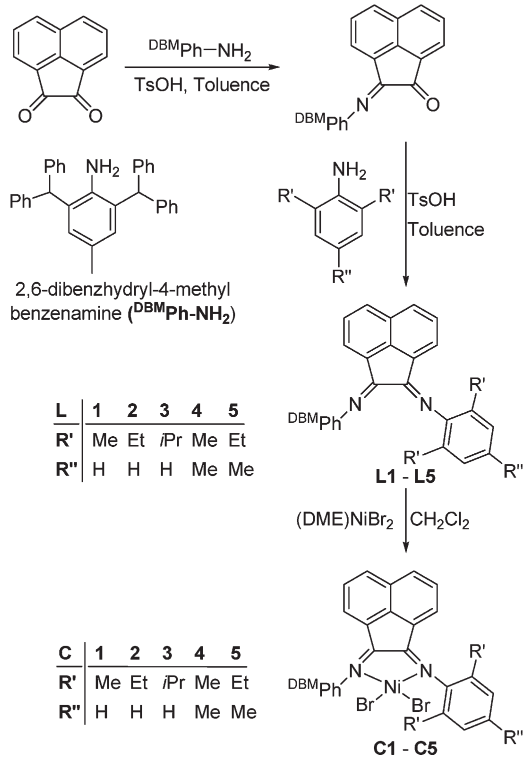
Scheme 1. Synthesis of Ligands (L1−L5) and Nickel Complexes (C1−C5)



2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of Ligands and Complexes. The stoichiometric condensation reaction of acenaphthylene-1,2-dione and 2,6-dibenzhydryl-4-methylaniline produced the 2-(2,6-dibenzhydryl-4-methylphenylimino)acenaphthylenone, which further reacted with various anilines to afford the unsymmetrical α-diimines 2,6-dibenzhydryl-*N*-(2-phenyliminoacenaphthylenylidene)-4-methylbenzenamine (**L1**−**L5**) (Scheme 1). All newly synthesized α-diimines (**L**) on reaction with nickel(II) dibromide in dichloromethane formed α-diimine nickel(II) dibromide complexes (**C1**−**C5**) in good yields (Scheme 1). The nickel complexes were characterized by IR spectra and elemental analysis.

2.2. X-ray Crystallographic Studies. Single crystals of complexes **C4** and **C5** suitable for X-ray diffraction analysis were grown by slow diffusion of diethyl ether into dichloromethane solutions. The molecular structures of complexes **C4** and **C5** were confirmed by single-crystal X-ray diffraction. The molecular structures are shown in Figures 1 and 2, respectively, and selected bond lengths and angles are tabulated in Table S1 of the Supporting Information. As shown in Figure 1, the coordination geometry of **C4** can be best described as a distorted tetrahedron, with the three atoms N1, N2, and Br2 forming the basal plane and the Br1 atom occupying the apical position. The nickel atom is 0.892 Å away from the basal plane. The plane composed by N1, N2, and Ni1 and the basal plane form a dihedral angle of 35.9°. The dihedral angles between the aryl ring on N1 and the basal plane and between the aryl ring on N2 and the basal plane are 49.5 and 48.6°, respectively. There is a fused five-membered ring of nickel and the ligand with an acute angle N1−Ni1−N2 of 83.03(14)° and bond distances Ni1−N1 = 2.040(3) Å and Ni1−N2 = 2.027(3) Å. The bond lengths N1−C12 and N2−C1 of the imino functions are 1.284(5) and 1.281(5) Å, respectively, both of which are typical of C═N double-bond character.

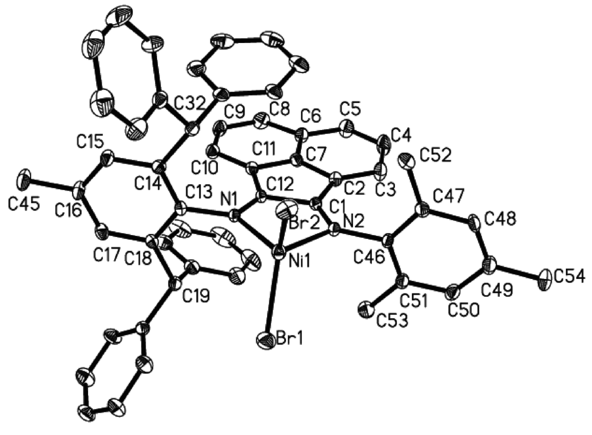


Figure 1. ORTEP drawing of **C4**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

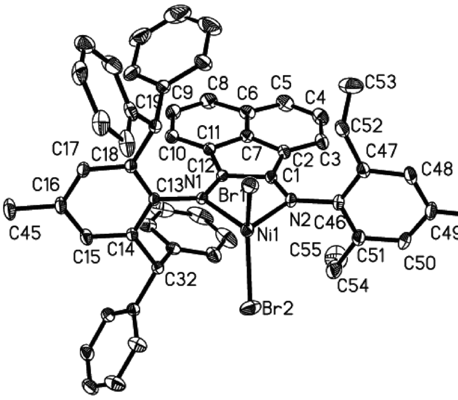


Figure 2. ORTEP drawing of **C5**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

In the structure of **C5**, the nickel atom is surrounded by an *N*-(2-(2,6-dibenzhydryl-4-methylphenylimino)acenaphthylenylidene)-2,6-diethyl-4-methylbenzenamine ligand and bound by two terminal bromides. Similar to the case for **C4**, the geometry of the four-coordinate complex can be described as a distorted tetrahedron, with the plane composed by the three atoms N1, N2, and Br2 as the basal plane and the Br1 atom occupying the apical position. The plane composed by N1, N2, and Ni1 and the basal plane form a dihedral angle of 35.6°. The dihedral angles between the aryl ring on N1 and the basal plane and between the aryl ring on N2 and the bottom plane are 51.4 and 52.1°, respectively, both greater than those observed for **C4**. The **C5** bond distances Ni1−N1 = 2.039(2) Å and Ni1−N2 = 2.010(3) Å are similar to those observed for **C4**. The bond lengths associated with the imino functions N1−C12 and N2−C1 are 1.291(4) and 1.286(4) Å, respectively.

2.3. Ethylene Polymerization. In order to determine the most suitable cocatalyst, initial investigations of procatalyst **C4** were conducted with various alkylaluminum reagents, such as ethylaluminum sesquichloride ($Et_3Al_2Cl_3$, EASC), methylaluminoxane

Table 1. Ethylene Polymerization by Procatalyst C4 with Various Cocatalysts[a]

entry	cocat.	Al/Ni	T/°C	t/min	activity/10^6 g of PE (mol of Ni)$^{-1}$ h^{-1}	M_w[b]/10^5 g mol^{-1}	M_w/M_n[b]	T_m[c]/°C
1	MAO	1000	20	30	3.30	12.78	21	91.8
2	MMAO	1000	20	30	trace			
3	Et_2AlCl	200	20	30	6.08	10.43	2.8	82.3
4	EASC	200	20	30	trace			

[a] Conditions: 1.5 μmol of Ni; 30 min; 10 atm of ethylene; total volume 100 mL. [b] Determined by GPC. [c] Determined by DSC.

Table 2. Catalytic Results of Ethylene Polymerization with C1−C5/Et_2AlCl[a]

entry	procat.	Al/Ni	T/°C	t/min	activity/10^6 g of PE (mol of Ni)$^{-1}$ h^{-1}	M_w[b]/10^5 g mol^{-1}	M_w/M_n[b]	T_m[c]/°C
1	**C4**	400	20	30	9.28	5.43	2.4	65.2
2	**C4**	500	20	30	10.7	5.55	2.2	65.2
3	**C4**	600	20	30	10.8	5.97	2.2	78.4
4	**C4**	700	20	30	10.6	6.08	2.5	79.7
5	**C4**	800	20	30	9.88	6.74	2.6	70.1
6	**C4**	1000	20	30	9.83	7.43	2.5	69.2
7	**C4**	600	40	30	6.36	4.62	2.3	48.7
8	**C4**	600	60	30	4.48	2.98	2.2	
9	**C4**	600	50	30	4.81	4.68	2.2	29.1
10	**C1**	600	20	30	9.95	4.72	2.4	56.2
11	**C2**	600	20	30	6.88	6.87	2.3	65.2
12	**C3**	600	20	30	10.9	9.42	2.7	49.1
13	**C5**	600	20	30	8.53	7.74	2.4	80.8
14	**C4**	600	20	5	13.0	5.63	2.2	58.7
15	**C4**	600	20	10	11.8	5.69	2.3	53.6
16	**C4**	600	20	20	10.9	5.81	2.4	52.9
17	**C4**	600	20	60	6.65	7.95	2.7	78.4

[a] Conditions: 1.5 μmol of Ni; 30 min; 10 atm of ethylene; total volume 100 mL. [b] Determined by GPC. [c] Determined by DSC.

(MAO), modified methylaluminoxane (MMAO), and diethylaluminum chloride (Et_2AlCl), at room temperature under 10 atm of ethylene (see Table 1). It was found that Et_2AlCl was found to be the most effective cocatalyst. Although the **C4**/MAO catalyst system did not present the dominant activities, it was observed to afford a diverse array of polymer products. For this reason, the catalytic behavior of **C4**/MAO was also investigated in detail.

*2.3.1. Ethylene Polymerization with **C1**−**C5**/Et_2AlCl System.* The catalytic behavior of complex **C4** was evaluated for optimum conditions in the presence of either Et_2AlCl or MAO. In the presence of Et_2AlCl, reaction parameters such as molar ratios of Et_2AlCl to nickel and reaction temperatures are collected in Table 2. From the data, it was observed that the catalytic activity was enhanced on increasing the Al/Ni ratio from 200 up to 600 (entry 3 in Table 1 and entries 1−3 in Table 2), and for the **C4**/Et_2AlCl catalyst system, the highest activity was 1.30×10^7 g of PE (mol of Ni)$^{-1}$ h^{-1} within 5 min (entry 14 in Table 2) and 1.08×10^7 g of PE (mol of Ni)$^{-1}$ h^{-1} within 30 min (entry 3 in Table 2). However, a slight decrease of activity was observed on further increasing the Al/Ni ratio from 600 to 1000 (entries 3−6 in Table 2). Thus, the most suitable molar ratio of Al to Ni was 600:1 (entry 3 in Table 2), while the best performance was observed at 20 °C (entries 3 and 7−9 in Table 2). Further elevating the temperature from 20 to 60 °C led to a marked decrease of activity, while simultaneously the molecular weights exhibited the reverse trend, which is similar to the situation previously observed for reported α-diimine catalyst systems.[16a−e] The other procatalysts were also found to have good activity for ethylene polymerization, and the data are summarized in Table 2.

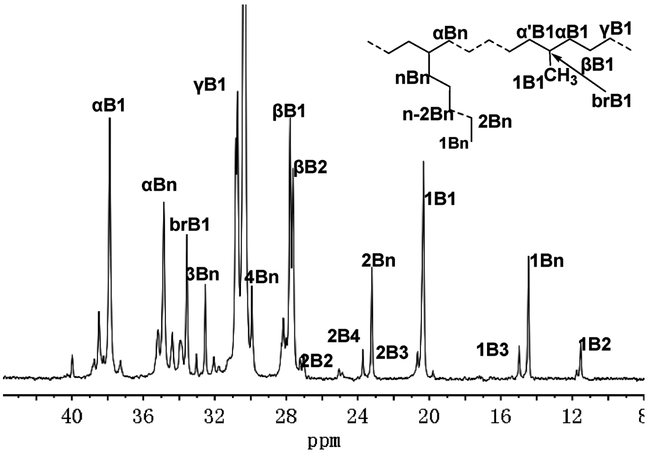


Figure 3. ^{13}C NMR spectrum of polyethylene prepared with catalyst **C4**/$AlEt_2Cl$ (entry 8 in Table 2).

The melting temperatures of the polyethylenes obtained were found to be lower than 81 °C. Such unusual properties were caused by the polyethylenes with high branches, which were confirmed by the ^{13}C NMR measurements. As shown in Figure 3, the number of branches was calculated according to the

Table 3. Catalytic Results of Ethylene Polymerization with C1−C5/MAO[a]

entry	procat.	Al/Ni	T/°C	T/min	activity/10^6 g of PE (mol of Ni)$^{-1}$ h^{-1}	$M_w{}^b/10^5$ g mol^{-1}	$M_w/M_n{}^b$	$T_m{}^c$/°C
1	**C4**	2000	20	30	7.21	nd	nd	57.2
2	**C4**	2500	20	30	8.94	6.18	2.4	81.7
3	**C4**	3000	20	30	9.32	6.99	2.5	75.3
4	**C4**	3500	20	30	6.34	7.62	2.6	75.8
5	**C4**	4000	20	30	4.08	8.13	3.1	90.3
6	**C4**	3000	40	30	5.41	5.63	2.4	60.2
7	**C4**	3000	60	30	4.37	3.67	2.2	36.5
8	**C4**	3000	50	30	4.90	3.53	2.4	92.2
9	**C1**	3000	20	30	9.23	6.74	2.5	90.8
10	**C2**	3000	20	30	7.73	6.77	2.6	69.7
11	**C3**	3000	20	30	9.39	7.45	2.5	62.7
12	**C5**	3000	20	30	1.89	7.44	2.7	76.2
13	**C4**	3000	20	5	10.6	5.76	2.5	69.2
14	**C4**	3000	20	10	10.2	5.84	2.5	49.6
15	**C4**	3000	20	20	9.60	6.02	2.6	81.2
16	**C4**	3000	20	60	6.10	8.85	3.3	90.8

[a] Conditions: 1.5 μmol of Ni; 30 min; 10 atm of ethylene; total volume: 100 mL. [b] Determined by GPC. [c] Determined by DSC.

literature,[23] and it was found that the polyethylene with 337 branches/1000 carbons (Figure 3) was obtained at 60 °C (entry 8 in Table 2), while the polyethylene with 99 branches/1000 carbons (Figure S1, Supporting Information) was obtained at 20 °C (entry 3 in Table 2). Using routine DSC procedures, the polyethylenes were heated during the first scan, and then cooled back down to room temperature, whereupon the kinetic properties remained for highly branched polyethylenes, which resulted in some of the T_m values obtained being quite low.

2.3.2. Ethylene Polymerization with ***C1*−*C5****/MAO System.* Using MAO as cocatalyst, all nickel procatalysts (**C1**−**C5**) also showed good catalytic activities toward ethylene polymerization, and the data are tabulated in Table 3. From the table, better activities were observed on increasing the Al/Ni molar ratio from 2000 to 3000 (entries 1−3 in Table 3). When the Al/Ni molar ratio is further increased to 4000, a slight decrease in the activity was observed. Similar to the case for the **C4**/Et_2AlCl catalytic system, the molecular weights and distributions both gradually increased with an increase in Al:Ni molar ratios for the **C4**/MAO catalytic system (entries 2−5 in Table 3). The best performance was observed at 20 °C (entry 3 and entries 6−8 in Table 3), and the molecular weights decreased upon an increase in the temperature (entries 3, 6, and 7 in Table 3). The polymerization activity, similar to that for the **C1**−**C5**/Et_2AlCl system, decreased in the order **C4** [2,4,6-tri(Me)] > **C5** [2,6-di(Et)-4-Me], **C3** [2,6-di(*i*-Pr)] > **C1** [2,6-di(Me)] > **C2** [2,6-di(Et)]. Again, as shown in the catalytic systems with the cocatalyst Et_2AlCl, the obtained polyethylenes with cocatalyst MAO are also highly branched, as reflected by the low T_m values measured.

In terms of the lifetime for both the **C4**/Et_2AlCl and **C4**/MAO systems, the ethylene polymerization was conducted over different time periods, namely 5, 10, 20, 30, and 60 min (entries 3 and 14−17 in Table 2 and entries 3 and 13−16 in Table 3). When the reaction time was increased from 5 to 30 min, the production followed an exponential increase (see Figure S2 in the Supporting Information), whereas on further prolonged reaction time, a distinct decrease of output was observed, suggesting that active species suffered from deactivation for reaction times over 30 min.

3. CONCLUSION

The synthesis and characterization of a class of nickel-based ethylene polymerization catalysts ligated by new bulky unsymmetrical α-diimines are described. Despite the fact that there have been many reported α-diimine systems in the literature, the unsymmetrical α-diimine presented herein represents a new research avenue for α-diimine catalytic systems. On treatment with the cocatalysts Et_2AlCl and MAO, these complexes afforded outstanding catalytic activity in the range of 10^7 g of PE (mol of Ni)$^{-1}$ h^{-1}, and the polyethylenes obtained exhibited a high degree of branching. Thus, the homopolymerization of ethylene by the current nickel procatalysts provided highly branched polyethylenes; the degree of branching varies at different temperatures. The use of the ligand systems described herein with other metals, as well as the polymerization of other monomers, will be reported separately.

4. EXPERIMENTAL SECTION

4.1. General Considerations. All manipulations of air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane, 3A) were purchased from Akzo Nobel Corp. Diethylaluminum chloride ($AlEt_2Cl$, 0.79 M in toluene) and ethylaluminum sesquichloride (EASC, 0.87 M in toluene) was purchased from Acros Chemicals. High-purity ethylene was purchased from Beijing Yansan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros, or local suppliers. NMR spectra were recorded on a Bruker DMX 400 MHz instrument at ambient temperature using TMS as an internal standard; δ values are given in ppm and *J* values in Hz. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 microanalyzer. Molecular weights and molecular weight distribution (MWD) of polyethylene were determined by a PL-GPC220 at 150 °C, with 1,2,4-trichlorobenzene as the solvent. Melting points of polyethylenes were measured from the second scanning run on a Perkin-Elmer DSC-7 differential scanning calorimetry

(DSC) analyzer under a nitrogen atmosphere; in the procedure, a sample of about 2.0−6.0 mg was heated to 160 °C at a rate of 10 °C/min and kept for 5 min at 160 °C to remove the thermal history and then cooled at a rate of 10 °C/min to 20 °C. ^{13}C NMR spectra of the polyethylenes were recorded on a Bruker DMX-300 MHz instrument at 135 °C in deuterated 1,2-dichlorobenzene with TMS as an internal standard.

4.2. Syntheses and Characterization. *4.2.1. 2-(2,6-Dibenzhydryl-4-methylphenylimino)acenaphthylenone.* A mixture of 2,6-diphenylmethyl-4-methylaniline (1.45 g, 3.3 mmol), acenaphthylene-1,2-dione (0.60 g, 3.3 mmol), and a catalytic amount of *p*-toluenesulfonic acid in toluene (80 mL) was refluxed for 6 h. After solvent evaporation at reduced pressure, the crude product was purified by column chromatography on silica with the eluent petroleum ether/dichloromethane (2/1 v/v) to afford 0.35 g of the red solid of the product in 17.6% isolated yield. Mp: 222−223 °C. IR (KBr; cm^{-1}): 3025.9 (w), 1722.6 (s), 1649.9 (m), 1595.3 (s), 1491.5 (s), 1446.6 (s), 1274.4 (m), 1071.2 (m), 1026.4 (s), 908.5 (m), 829.2 (m), 776.9 (s), 743.4 (s), 694.7 (vs). Anal. Calcd for $C_{45}H_{33}NO$ (603.75): C, 89.52; H, 5.51; N, 2.32. Found; C, 89.22; H, 5.77; N, 1.99. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.029 (t, J = 6.56, 2H), 7.71 (m, 2H), 7.26−7.22 (m, 4H), 7.18 (d, J = 6.98, 2H), 7.05 (d, 5H), 6.86 (d, 4H), 6.79 (s, 2H), 6.60 (t, 4H), 6.43 (t, 2H), 6.14 (d, J = 7.08, 1H), 5.43 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 189.91, 162.50, 146.08, 143.11, 142.61, 141.91, 133.36, 131.94, 131.89, 129.83, 129.59, 128.84, 128.54, 128.29, 127.93, 127.13, 126.33, 125.64, 124.06, 121.67, 52.29, 21.67.

*4.2.2. Synthesis of 2,6-Dibenzhydryl-N-(2-phenyliminoacenaphthylenylidene)-4-methylbenzenamine (**L1**−**L5**)*

4.2.2.1. 2,6-Dibenzhydryl-N-(2-(2,6-dimethylphenylimino)acenaphthylenylidene)-4-methylbenzenamine (L1). A solution of 2-(2,6-dibenzhydryl-4-methylphenylimino)acenaphthylenone (0.34 g, 0.56 mmol), 2,6-dimethylaniline (0.075 g, 0.62 mmol), and a catalytic amount of *p*-toluenesulfonic acid in toluene (50 mL) was mixed and refluxed for 10 h. The solution was evaporated at reduced pressure. The residual solids were further purified by silica column chromatography (8/1 petroleum ether/ethyl acetate) to afford 0.15 g of **L1** (yellow, 37.7% yield). Mp: 211−212 °C. IR (KBr; cm^{-1}): 3024.6 (w), 2915.6 (w), 1735.0 (m), 1664.5 (m), 1592.7 (m), 1493.8 (s), 1441.4 (s), 1233.3 (s), 1034.0 (s), 921.0 (m), 831.8 (m), 763.8 (vs), 739.8 (s). Anal. Calcd for $C_{53}H_{42}N_2$ (706.91): C, 90.05; H, 5.99; N, 3.96. Found; C, 89.77; H, 5.68; N, 4.21. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.72 (d, J = 8.20, 1H), 7.58 (d, J = 8.25, 1H), 7.26−7.23 (m, 5H), 7.17 (m, 4H), 7.12−7.06 (m, 5H), 6.99 (t, J = 7.80, 1H), 6.94 (d, J = 7.49, 4H), 6.79 (s, 2H), 6.60 (t, J = 7.38, 4H), 6.53 (d, J = 7.12, 1H), 6.42 (t, J = 7.33, 2H), 6.10 (d, J = 7.08, 1H), 5.30 (s, 2H), 2.27 (s, 3H), 2.21 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.58, 161.52, 149.46, 146.88, 143.43, 142.04, 140.09, 132.75, 132.38, 129.99, 129.71, 128.91, 128.81, 128.45, 128.26, 127.84, 127.60, 127.01, 126.22, 125.57, 124.96, 124.34, 123.82, 121.84, 52.40, 21.69, 18.29.

4.2.2.2. 2,6-Dibenzhydryl-N-(2-(2,6-diethylphenylimino)acenaphthylenylidene)-4-methylbenzenamine (L2). Using the same procedure as for the synthesis of **L1**, **L2** was obtained as a yellow powder in 32.8% yield (0.43 g). Mp: 214−215 °C. IR (KBr; cm^{-1}): 3025.5 (w), 2928.4 (w), 1739.3 (m), 1672.5 (m), 1593.8 (m), 1494.0 (s), 1441.7 (vs), 1235.0 (vs), 1036.4 (s), 920.6 (m), 831.0 (m), 762.1 (vs), 739.3 (s). Anal. Calcd for $C_{55}H_{46}N_2$ (734.97): C, 89.88; H, 6.31; N, 3.81. Found; C, 89.44; H, 6.17; N, 4.03. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.70 (d, J = 8.20, 1H), 7.55 (d, J = 8.23, 1H), 7.28−7.17 (m, 10H), 7.13 (d, J = 7.36, 4H), 7.95 (d, J = 7.16, 5H), 6.82 (s, 2H), 6.60 (t, J = 7.31, 4H), 6.53 (d, J = 7.06, 1H), 6.42 (t, J = 7.22, 2H), 6.03 (d, J = 7.04, 1H), 5.66 (s, 2H), 2.70 (m, 2H), 5.54 (m, 2H), 2.29 (s, 3H), 1.18 (t, J = 7.47, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.65, 161.81, 148.52, 146.97, 143.65, 141.95, 140.10, 132.74, 132.38, 130.82, 129.94, 129.72, 128.99, 128.71, 128.22, 127.87, 127.34, 127.02, 126.27, 126.21, 125.60, 124.40, 124.18, 122.40, 52.34, 24.60, 21.69, 14.54.

4.2.2.3. 2,6-Dibenzhydryl-N-(2-(2,6-diisopropylphenylimino)acenaphthylenylidene)-4-methylbenzenamine (L3). Using the same procedure as for the synthesis of **L1**, **L3** was obtained as a yellow powder in 33.7% yield (0.34 g). Mp: 228−229 °C. IR (KBr; cm^{-1}): 3025.6 (w), 2958.4 (m), 1737.6 (s), 1650.8 (m), 1592.4 (s), 1493.0 (s), 1442.5 (s), 1238.8 (vs), 1039.0 (s), 927.1 (m), 829.6 (m), 764.1 (s), 744.1 (s). Anal. Calcd for $C_{57}H_{50}N_2$ (763.02): C, 89.72; H, 6.60; N, 3.67. Found: C, 89.33; H, 6.80; N, 3.44. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.67 (d, J = 8.22, 1H), 7.51 (d, J = 8.25, 1H), 7.29−7.24 (m, 7H), 7.22−7.17 (m, 3H), 7.12 (d, J = 7.45, 4H), 6.94−6.88 (m, 5H), 6.81 (s, 2H), 6.57 (t, J = 7.40, 4H), 6.45−6.37 (m, 3H), 5.93 (d, J = 7.10, 1H), 5.65 (s, 2H), 3.18 (m, 2H), 2.28 (s, 3H), 1.29 (d, J = 7.05, 6H), 1.02 (d, J = 6.78, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.78, 162.22, 147.28, 147.01, 143.77, 141.85, 140.13, 135.86, 132.75, 132.44, 129.90, 129.72, 129.02, 128.72, 128.18, 127.91, 127.16, 129.79, 126.17, 125.61, 124.61, 124.46, 123.70, 123.01, 52.27, 28.63, 24.39, 23.87, 21.67.

4.2.2.4. 2,6-Dibenzhydryl-N-(2-(2,4,6-trimethylphenylimino)acenaphthylenylidene)-4-methylbenzenamine (L4). Using the same procedure as for the synthesis of **L1**, **L4** was obtained as a yellow powder in 29.7% yield (0.22 g). Mp: 231−232 °C. IR (KBr; cm^{-1}): 3025.9 (w), 2914.7 (m), 1737.3 (s), 1664.7 (m), 1594.4 (m), 1493.2 (s), 1441.4 (s), 1235.2 (vs), 1036.8 (s), 918.6 (m), 837.0 (m), 765.8 (s), 738.8 (s). Anal. Calcd for $C_{54}H_{44}N_2$ (720.94): C, 89.96; H, 6.15; N, 3.89. Found: C, 89.55; H, 5.98; N, 4.11. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.71 (d, J = 8.22, 1H), 7.57 (d, J = 8.20, 1H), 7.29−7.22 (m, 5H), 7.19−7.15 (m, 2H), 7.11 (d, J = 7.46, 4H), 6.99 (m, 3H), 6.93 (d, J = 7.55, 4H), 6.79 (s, 2H), 6.60 (m, 5H), 6.42 (t, J = 7.22, 2H), 6.10 (d, J = 7.13, 1H), 5.61 (s, 2H), 2.38 (s, 3H), 2.27 (s, 3H), 2.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.58, 161.63, 146.88, 143.38, 142.01, 140.02, 132.96, 132.64, 132.35, 129.95, 129.67, 129.11, 128.84, 128.63, 128.21, 128.05, 127.79, 127.54, 126.92, 126.16, 125.50, 124.67, 124.23, 121.81, 52.33, 21.65, 21.05, 18.17.

4.2.2.5. 2,6-Dibenzhydryl-N-(2-(2,6-diethyl-4-methylphenylimino)acenaphthylenylidene)-4-methylbenzenamine (L5). Using the same procedure as for the synthesis of **L1**, **L5** was obtained as a yellow powder in 30.4% yield (0.41 g). Mp: 218−219 °C. IR (KBr; cm^{-1}): 3024.2 (w), 2912.9 (w), 1738.3 (m), 1660.2 (m), 1594.5 (m), 1493.84 (s), 1442.0 (vs), 1234.9 (vs), 1035.6 (s), 917.9 (m), 834.1 (m), 767.2 (s), 740.9 (s). Anal. Calcd for $C_{56}H_{48}N_2$ (748.99): C, 89.80; H, 6.46; N, 3.74. Found: C, 89.67; H, 6.33; N, 3.92. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.69 (d, J = 8.25, 1H), 7.53 (d, J = 8.28, 1H), 7.26−7.33 (m, 5H), 7.17 (m, 2H), 7.11 (d, J = 7.56, 4H), 7.02 (s, 2H), 6.93 (m, 5H), 6.80 (s, 2H), 6.58 (t, 5H), 6.40 (t, J = 7.35, 2H), 6.01 (d, J = 7.16, 1H), 5.62 (s, 2H), 2.64 (m, 2H), 2.49 (m, 2H), 2.43 (s, 3H), 2.27 (s, 3H), 1.15 (t, J = 7.52, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 163.70, 161.96, 147.00, 145.96, 143.64, 141.95, 140.06, 133.30, 132.66, 132.39, 130.63, 129.93, 129.71, 128.95, 128.57, 128.19, 127.85, 127.30, 127.04, 126.96, 126.18, 125.56, 124.33, 122.41, 52.31, 24.57, 21.67, 21.39, 14.65.

*4.2.3. Synthesis of the Tridentate Nickel Complexes **C1**−**C5**.* The complexes **C1**−**C5** were synthesized by the reaction of (DME)$NiBr_2$ with the corresponding ligands in dichloromethane. A typical synthetic procedure for **C1** is described as follows. The ligand **L1** (0.146 g, 0.21 mmol) and (DME)$NiBr_2$ (0.068 g, 0.22 mmol) were added to a Schlenk tube together with 10 mL of dried dichloromethane. The reaction mixture was then stirred for 8 h at room temperature, and absolute diethyl ether (10 mL) was added to precipitate the complex. The precipitate was washed with diethyl ether and dried under vacuum to obtain a red powder of **C1** in 83.3% (0.16 g) yield. IR (KBr; cm^{-1}): 3025.7 (w), 2964.3 (w), 1645.1 (w), 1601.3 (m), 1580.9 (s), 1494.2 (m), 1444.1 (s), 1292.9 (m), 1187.7 (w), 1082.2 (m), 1031.5 (m), 826.6 (m), 772.2 (vs), 747.8 (s). Anal. Calcd for $C_{53}H_{42}Br_2N_2Ni$ (925.42): C, 68.79; H, 4.57; N, 3.03. Found: C, 68.40; H, 4.76; N, 3.31.

4.2.3.1. Data for C2. Yield: 86.8% (0.16 g), red powder. IR (KBr; cm^{-1}): 3028.8 (w), 2967.9 (w), 1649.0 (w), 1629.6 (m), 1582.5

(s), 1492.7 (s), 1442.9 (s), 1287.9 (m), 1178.6 (m), 1075.5 (m), 1029.4 (m), 827.4 (m), 768.7 (vs), 744.4 (s). Anal. Calcd for $C_{55}H_{46}Br_2N_2Ni$ (953.47): C, 69.28; H, 4.86; N, 2.94. Found: C, 68.89; H, 4.59; N, 3.13.

4.2.3.2. Data for C3. Yield: 85.9% (0.091 g), red powder. IR (KBr; cm^{-1}): 3024.0 (w), 2967.9 (m), 1646.0 (w), 1619.9 (m), 1581.6 (s), 1493.4 (s), 1444.3 (s), 1290.0 (m), 1179.9 (m), 1078.6 (w), 1036.9 (m), 828.8 (m), 769.9 (vs), 745.3 (s). Anal. Calcd for $C_{57}H_{50}Br_2N_2Ni$ (981.52): C, 69.75; H, 5.13; N, 2.85. Found: C, 69.57; H, 5.03; N, 3.22.

4.2.3.3. Data for C4. Yield: 82.4% (0.19 g), red powder. IR (KBr; cm^{-1}): 3025.5 (w), 2973.0 (w), 1645.4 (w), 1602.1 (m), 1585.1 (s), 1493.6 (s), 1444.1 (s), 1294.1 (m), 1198.9 (w), 1074.9 (w), 1031.5 (m), 825.3 (m), 767.3 (vs), 742.9 (s). Anal. Calcd for $C_{54}H_{44}Br_2N_2Ni$ (939.44): C, 69.04; H, 4.72; N, 2.98. Found: C, 69.31; H, 4.51; N, 3.16.

4.2.3.4. Data for C5. Yield: 75.0% (0.15 g), red powder. IR (KBr; cm^{-1}): 3022.7 (w), 2968.4 (w), 1652.3 (m), 1621.9 (s), 1583.3 (s), 1493.8 (s), 1445.0 (s), 1290.4 (m), 1182.4 (w), 1075.8 (w), 1030.8 (m), 829.1 (m), 770.0 (vs), 742.1 (s). Anal. Calcd for $C_{56}H_{48}Br_2N_2Ni$ (967.5): C, 69.52; H, 5.00; N, 2.90. Found: C, 69.18; H, 5.14; N, 3.10.

4.3. X-ray Crystallographic Studies. Single crystals of **C4** and **C5** suitable for X-ray diffraction analysis were obtained by laying diethyl ether on the dichloromethane solution at room temperature. With graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 173(2) K, cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.[24] Details of the X-ray structure determinations and refinements are provided in Table S2 of the Supporting Information.

■ ASSOCIATED CONTENT

S **Supporting Information.** Selected bond lengths and angles (Table S1) and structure refinement details for **C4** and **C5** (Table S2), the ^{13}C NMR spectrum of polyethylene prepared with catalyst **C4**/$AlEt_2Cl$ (entry 3 in Table 2, Figure S1), the output of **C4**/Et_2AlCl and **C4**/MAO systems over different reaction times (Figure S2), figures giving all GPC curves regarding the data of Tables 1 and 2, and CIF files giving X-ray crystal structure data of nickel complexes **C4** and **C5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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