

# Synthesis, Molecular Structure, and Solution-Dependent Behavior of Nickel Complexes Chelating Anilido–Imine Donors and Their Catalytic Activity toward Olefin Polymerization

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A series of novel nickel complexes (**1–4**) bearing anilido–imine ligands,  $[(Ar^1N=CHC_6H_4-NAr^2)NiBr]_2$  ( $Ar^1 = Ar^2 = 2,6$ -dimethylphenyl, **1**;  $Ar^1 = 2,6$ -dimethylphenyl,  $Ar^2 = 2,6$ -diisopropylphenyl, **2**;  $Ar^1 = Ar^2 = 2,6$ -diisopropylphenyl, **3**;  $Ar^1 = 2,6$ -diisopropylphenyl,  $Ar^2 = 2,6$ -dimethylphenyl, **4**), have been synthesized and characterized. The solid-state structures of the complexes **1**, **2**, and **4** were confirmed by X-ray single-crystal analyses to be in the form of a dinuclear and bromine-bridged structure. However, there is an equilibrium that shifts between the monomer and dimer in solution, which has been monitored using  $^1H$  NMR and UV–vis spectrophotometry. The thermodynamic parameters for the equilibria were calculated to be  $\Delta H = +13.68$  kJ/mol and  $\Delta S = 40.32$  J/(mol K) for **1** and  $\Delta H = +8.35$  kJ/mol and  $\Delta S = 15.21$  J/(mol K) for **3**. All nickel complexes show low activities for ethylene oligomerization with MAO as cocatalyst but high catalytic activities for norbornene polymerization in the presence of MAO.

## Introduction

Over the past decade, late-transition-metal catalysts for olefin polymerization have received increasing attraction, for they are much less oxophilic and more tolerant of polar functional groups than the catalysts ordinarily used.<sup>1</sup> Brookhart and his collaborators successfully developed bulky  $\alpha$ -diimine nickel and palladium complexes, which show high catalytic activity for  $\alpha$ -olefin polymerization.<sup>1a</sup> Subsequently,  $\alpha$ -diimine nickel and palladium complexes chelating five-membered rings were fully investigated in  $\alpha$ -olefin polymerization.<sup>1,2</sup> Feldman et al. reported that nickel and palladium complexes chelating six-membered neutral  $\beta$ -diketimine ligands showed less activity for ethylene polymerization than  $\alpha$ -diimine nickel and palladium complexes, due to the change from a five- to six-

membered chelate ring.<sup>3</sup> Later, late-transition-metal complexes chelating six-membered rings were less frequently reported until neutral nickel complexes chelating salicylaldimine ligands were reported by the Grubbs group to have high activity in polymerizing olefin and polar monomer.<sup>4,5</sup> Recently, six-membered anionic  $\beta$ -diketiminate ligands has been dramatically applied in bioinorganic and transition-metal chemistry,<sup>6,7</sup> and bulky  $\beta$ -diketiminate nickel complexes have been prepared.<sup>7c,e</sup> Our groups and others have also found that some  $\beta$ -diketiminate nickel complexes show good activity toward polymerizations of norbornene and ethylene.<sup>8</sup>

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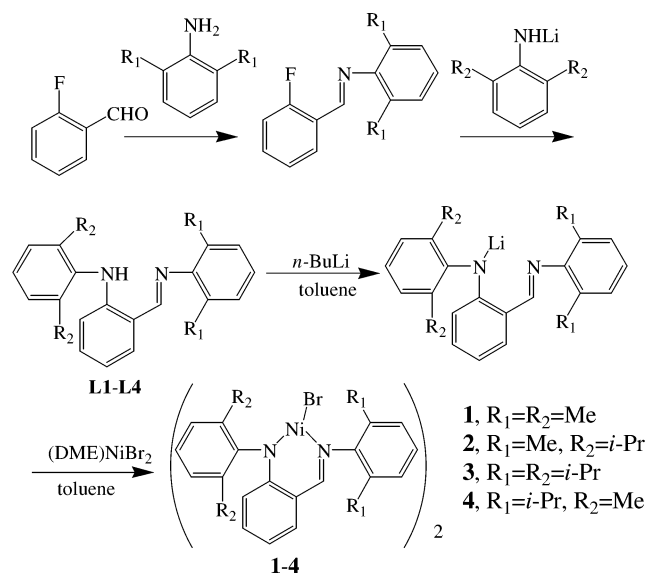
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## Scheme 1. Preparation of Nickel Complexes 1–4



In a comparison of salicylaldimine ligands with  $\beta$ -diketiminate ligands, the former have better conjugation and more easily modified features than the latter, but  $\beta$ -diketiminate ligands have greater steric effect, because two substituted aryl rings attached directly to nitrogen atoms are close to the metal center. When the steric effect of the  $\beta$ -diketiminate ligand is combined with the more easily modified features of the salicylaldimine ligand, the result could be that bulky anilido-imine compounds would find application in many areas of inorganic and organometallic chemistry. More recently, it has been reported that organoyttrium cations chelating bulky anilido-imine ligands showed more stability than  $\beta$ -diketiminato yttrium complexes.<sup>9</sup>

Herein the present contribution first reports the syntheses and solid-state structure characterizations of nickel complexes chelating bulky anilido-imine ligands and investigates their interesting solution behavior. Additionally, preliminary results from the complexes catalyzing ethylene and norbornene polymerizations after activation with methylaluminumoxane (MAO) are also shown.

## Results and Discussion

**Ligands and Complex Syntheses.** The three new anilido-imine ligands **L1**, **L2**, and **L4** were synthesized, but **L3** has been reported before.<sup>9</sup> A general synthetic route for these complexes is shown in Scheme 1. The imine formation occurs smoothly at room temperature, using the corresponding 2,6-substituted anilines and

Table 1. Crystallographic Data for Complexes 1, 2, and 4

	1	2	4
empirical formula	$C_{46}H_{46}Br_2-N_4Ni_2$	$C_{54}H_{62}Br_2-N_4Ni_2$	$C_{54}H_{62}Br_2-N_4Ni_2$
formula wt	932.11	1044.32	1044.32
temp (K)	293(2)	293(2)	293(2)
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
<i>a</i> (Å)	9.208(3)	9.008(1)	13.674(5)
<i>b</i> (Å)	11.424(3)	11.122(1)	13.350(5)
<i>c</i> (Å)	20.779(6)	13.541(2)	16.997(7)
$\alpha$ (deg)	90	73.925(2)	90
$\beta$ (deg)	100.503(5)	6.381(2)	125.038(6)
$\gamma$ (deg)	90	84.357(2)	90
<i>V</i> (Å <sup>3</sup> )	2149.2(11)	1266.1(3)	2540.6(16)
<i>Z</i>	2	1	2
<i>D<sub>t</sub></i> (Mg/m <sup>3</sup> )	1.440	1.370	1.365
abs coeff (mm <sup>-1</sup> )	2.771	2.36	2.352
<i>F</i> (000)	952	540	1080
cryst size (mm)	0.49 × 0.44 × 0.31	0.50 × 0.20 × 0.07	0.49 × 0.42 × 0.35
$\theta$ range (deg)	1.99–27.05	1.6–27.1	1.82–27.06
index ranges	–11 ≤ <i>h</i> ≤ 11 –6 ≤ <i>k</i> ≤ 14 –26 ≤ <i>l</i> ≤ 26	–11 ≤ <i>h</i> ≤ 11 –14 ≤ <i>k</i> ≤ 14 –17 ≤ <i>l</i> ≤ 17	–17 ≤ <i>h</i> ≤ 17 –11 ≤ <i>k</i> ≤ 17 –21 ≤ <i>l</i> ≤ 16
no. of params	184	282	286
goodness of fit on <i>F</i> <sup>2</sup>	1.053	1.00	1.025
final <i>R</i> indices ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) <sup>a</sup>	0.0560, 0.1458	0.033, 0.078	0.0313, 0.0706
<i>R</i> indices (all data) <sup>a</sup>	0.0738, 0.1587	0.059, 0.090	0.0529, 0.0790
largest diff peak and hole (e/Å <sup>-3</sup> )	1.257, –0.967	0.37, –0.38	0.552, –0.352

$$^a R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}; R_w = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}$$

*o*-fluorobenzaldehyde. In the second step, the anilido-imine ligands can be obtained via a nucleophilic aromatic displacement of fluorine using LiN(H)Ar. Although both of the reagents are reasonably sterically bulky, the reaction occurs in good yield and is no doubt aided by the electron-withdrawing nature of the neighboring imine group. It is noteworthy that the steric bulkiness of the ligands could be controlled easily by changing various bulky arylamines, and nonsymmetric ligands also could be synthesized by using various arylamines at each step.<sup>10</sup> All of these ligands have been confirmed by EIMS, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analyses.

After the anilido-imine ligands were treated with *n*-butyllithium in toluene, 1.1 equiv of (1,2-dimethoxyethane)nickel(II) bromide ((DME)NiBr<sub>2</sub>) was added to the solutions and the nickel complexes 1–4 were obtained as dark green solids. The structures of anilido-imino nickel complexes 1–4 were confirmed by elemental analyses and EIMS and <sup>1</sup>H NMR spectra (see the Experimental Section).

**Structural Features.** Crystals of complexes 1, 2, and 4 suitable for single-crystal X-ray diffraction analyses were grown from their hexane/toluene solutions. The data collection and refinement data of the analyses are summarized in Table 1. ORTEP diagrams are given in Figures 1–3, respectively.

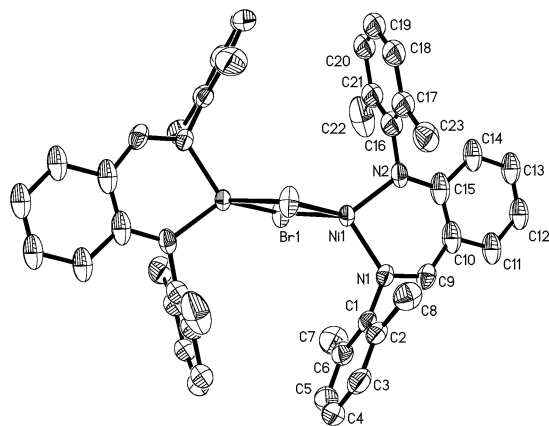
These three complexes exist as dimers in the solid state with tetrahedral geometries about nickel and a crystallographic *C*<sub>2</sub> axis of symmetry that makes the two units equivalent. As reported in the literature,<sup>3,7c</sup> the nickel complex chelating a neutral  $\beta$ -diketimine ligand has a nonplanar boat conformation, but the  $\beta$ -diketimi-

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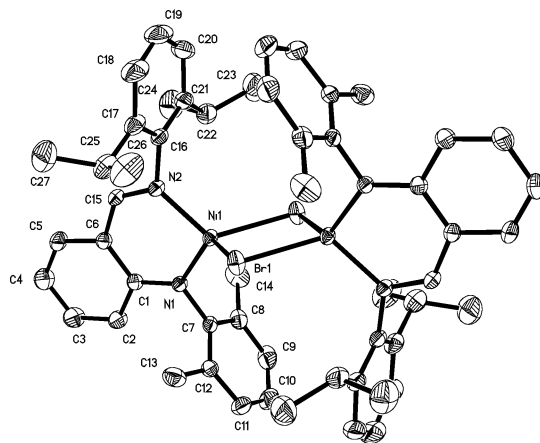
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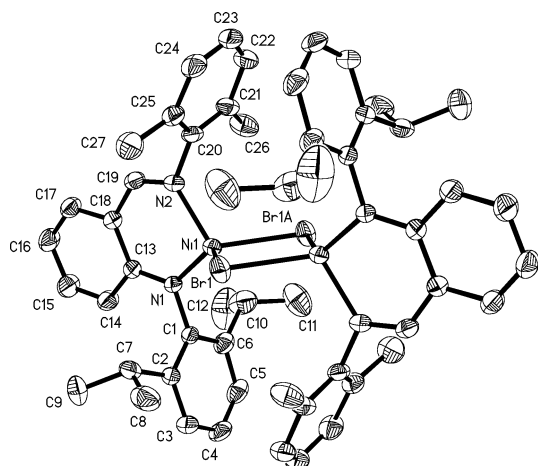
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**Figure 1.** ORTEP plot of complex **1**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)–N(2), 1.886(4); Ni(1)–N(1), 1.942(4); Ni(1)–Br(1)#1, 2.4135(8); Ni(1)–Br(1), 2.4464(8); N(2)–Ni(1)–N(1), 94.28(17); N(2)–Ni(1)–Br(1)#1, 124.43(15); N(1)–Ni(1)–Br(1)#1, 119.07(12); N(2)–Ni(1)–Br(1), 115.63(12); N(1)–Ni(1)–Br(1), 114.48(11); Br(1)#1–Ni(1)–Br(1), 90.74(3); Ni(1)#1–Br(1)–Ni(1), 89.26(3); C(9)–N(1)–Ni(1), 122.0(4); C(1)–N(1)–Ni(1), 120.5(3); C(15)–N(2)–Ni(1), 127.0(4); C(16)–N(2)–Ni(1), 113.6(4).



**Figure 3.** ORTEP plot of complex **4**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)–Br(1), 2.4415(7); Ni(1)–Br(1)#1, 2.4481(9); Ni(1)–N(1), 1.8861(18); Ni(1)–N(2), 1.9440(18); N(1)–Ni(1)–N(2), 94.32(8); N(1)–Ni(1)–Br(1), 120.26(6); N(2)–Ni(1)–Br(1), 116.23(6); N(1)–Ni(1)–Br(1)#1, 119.74(6); N(2)–Ni(1)–Br(1)#1, 119.98(6); Br(1)–Ni(1)–Br(1)#1, 88.81(3); Ni(1)–Br(1)–Ni(1)#1, 91.19(3); C(1)–N(1)–Ni(1), 128.70(15); C(7)–N(1)–Ni(1), 113.72(14); C(15)–N(2)–Ni(1), 123.36(16); C(16)–N(2)–Ni(1), 121.73(15).



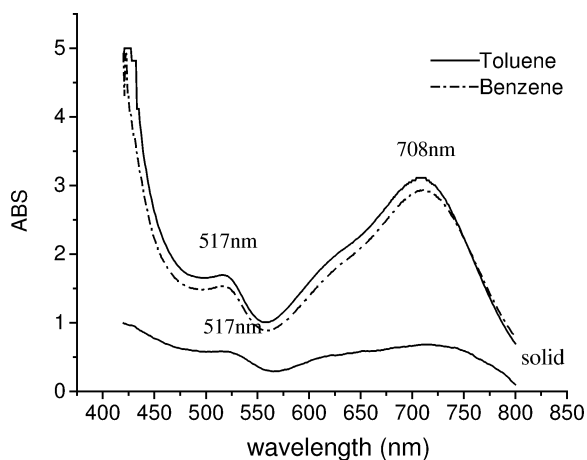
**Figure 2.** ORTEP plot of complex **2**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)–Br(1)A, 2.4520(5); Ni(1)–Br(1), 2.4468(4); Ni(1)–N(1), 1.888(2); Ni(1)–N(2), 1.951(2); Ni(1)–Br(1)–Ni(1)A, 92.71(1); Br(1)–Ni(1)–Br(1)A, 87.29(2); Br(1)–Ni(1)–N(1), 124.27(6); Br(1)–Ni(1)–N(2), 112.00(6); Br(1)A–Ni(1)–N(1), 128.18(6); Br(1)–Ni(1)–N(2), 112.38(6); N(1)–Ni(1)–N(2), 93.76(9); C(13)–N(1)–Ni(1), 128.7(2); C(1)–N(1)–Ni(1), 114.9(2); C(19)–N(2)–Ni(1), 124.3(2); C(20)–N(2)–Ni(1), 119.1(2).

nato nickel complex has a planar  $\beta$ -diketiminato skeleton. Similar to the  $\beta$ -diketiminato nickel complex, the anilido–imine skeleton also is a plane, but the benzene ring plane slightly swings the chelate plane (N1CCCN2). The interplanar angle between the benzene ring and the chelate plane is 4.8° for **1**, 2.1° for **2**, and 1.6° for **4**, respectively. The nickel atom lies 0.1416 Å out of the chelate plane for **1**, 0.130 Å for **2**, and 0.120 Å for **4**, respectively. Unlike the  $\beta$ -diketiminato complexes, the anilido–imino complexes are more localized and the two nitrogens bond to nickel with different bond lengths, and the N(amine)–Ni bond lengths are invariably shorter than the N(imine)–Ni bond lengths. The steric effects of the two N–aryl groups upon the nickel atom are also

unbalanced, owing to the difference in distance. The complex **2** contains a more bulky aryl group attached to the aniline than does the complex **4**, implying that there is a more crowded steric environment of the Ni atom for **2** than for **4**, even though these two complexes have the same composition. Though there is an unbalanced steric effect of the N-aryl groups, the bite angles (N–Ni–N) of the complexes are nearly the same. The Ni–Br distances are longer than typical Ni<sup>II</sup>–Br bonds.<sup>3</sup> The planes (Ni–Br–Ni) slightly deviate from a rectangle. The bite angle (Br–Ni–Br) is slightly less than 90° (87.29(1)° for **2** and 88.81(3)° for **4**). In contrast to complexes **2** and **4**, the bite angle (Br–Ni–Br) of **1** is slightly more 90° (90.74(3)°), which resulted from the different steric effects of 2,6-substituents. The Ni–Ni distances of complexes are over 3 Å, suggesting that there is no direct metal–metal interaction.

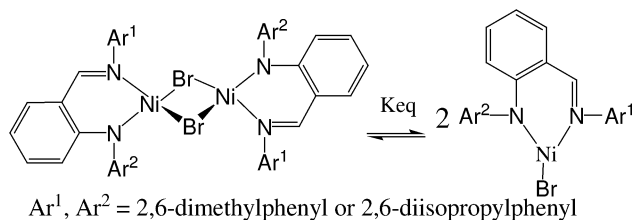
**Properties of Nickel Complexes in Solution.** The nickel complexes are sensitive to air and moisture and show interesting solvent-dependent behavior. In the solid state, these nickel complexes are dark green. However, dissolution in toluene, benzene, and methylene chloride gave a green solution. At the same concentration and temperature, the color of the anilido–imino nickel complex **1** solution persists longer than that of **3**, indicating that complex **3** is more unstable because of the bulky 2,6-substituents.

Though anilido–imino nickel complexes are four-coordinate dinuclear species in the solid state that exhibit an electronic absorption at  $\lambda_{\max}$  517 nm in UV–vis spectrophotometry (see Figure 4), there is an equilibrium that shifts between the three-coordinate monomer and four-coordinate dimer in solution (Scheme 2), which could be observed by UV–vis spectrophotometry. Figure 4 shows UV–vis spectra of nickel complex **1** in different solvents. There is a weak electronic absorption at 517 nm (dimer) and an intense electronic absorption at 708 nm (monomer), which support the monomer/dimer equilibrium in solution.



**Figure 4.** UV-vis spectra of **1** in various solvents. The solid-state spectrum is on an arbitrary scale.

### Scheme 2. Monomer/Dimer Equilibria of Anilido–Imino Nickel Complexes



$^1\text{H}$  NMR spectra also further explain this equilibrium. Similar to  $\beta$ -diketiminato nickel complexes,<sup>6d,7c</sup> the anilido–imino nickel complexes exhibit strongly broadened  $^1\text{H}$  NMR spectra from 60 to  $-90$  ppm, due to their paramagnetism. As a result of the paramagnetism effect, the four protons of the backbone benzene ring shifted intensely upfield, but the protons of the substituted aryl ring shifted to low field, and the proton of imine intensely shifted to low field to  $\sim 50$  ppm. In the spectra of the complexes, a series of broadened major signals and minor signals were observed. These signals can be clearly divided into two sets: one set is assigned to the monomer and the other set to the dimer. As an example, Figure 5 shows the  $^1\text{H}$  NMR spectrum of complex **1** in  $\text{C}_6\text{D}_6$  at  $18^\circ\text{C}$ , and the assignments of signals are summarized in Table 2. The intensity ratio of the monomer signals to dimer signals is 5:1, implying the molar ratio of monomer to dimer in 10:1 under this conditions.

To further examine these equilibria in solution, we monitored  $^1\text{H}$  NMR spectra of complexes **1** and **3** at temperatures of  $-15$  to  $50^\circ\text{C}$  in toluene- $d_8$  solution. Above  $70^\circ\text{C}$ , only monomer was detected at the concentration used. The equilibrium constants for the dissociation of dimer into monomer ( $K_{\text{eq}}$ ; see Scheme 2) were obtained from the data of  $^1\text{H}$  NMR spectra (see Table 3). The  $\ln K_{\text{eq}}$  vs  $1/T$  plots are shown in Figure 6. On the basis of the data of  $K_{\text{eq}}$  at various temperatures, the values of enthalpy and entropy can be calculated according to the van't Hoff equation<sup>11,12</sup> to be  $\Delta H =$

**Table 2.**  $^1\text{H}$  NMR Chemical Shifts (ppm) of the Complex **1** in  $\text{C}_6\text{D}_6$  at  $18^\circ\text{C}$

proton	chem shift (ppm)	
	monomer	dimer
imine (CH=N)	49.99	55.13
substituent methyl (Me)	43.63, 38.29	38.68, 32.43
<i>m</i> -aryl	46.09, 32.56	47.67, 31.93
<i>p</i> -aryl	29.12, 7.02	31.93, 10.57
backbone benzene	$-13.00, -28.40,$ $-59.47, -74.10$	$-12.90, -29.73,$ $-76.06, -86.57$

**Table 3.** Equilibrium Constants ( $K_{\text{eq}}$ ) for the Dissociation of Dimer into Monomer at Various Temperatures in Toluene- $d_8$  Solution<sup>a</sup>

temp ( $^\circ\text{C}$ )	$K_{\text{eq}}$	
	<b>1</b>	<b>3</b>
$-15$	0.2308	$-2.0541$
$0$	0.2880	$-1.8326$
$28$	0.5217	$-1.5686$
$50$	0.8181	$-1.2384$

<sup>a</sup> Concentrations of complexes are 45 mM for **1** and 25 mM for **3**.

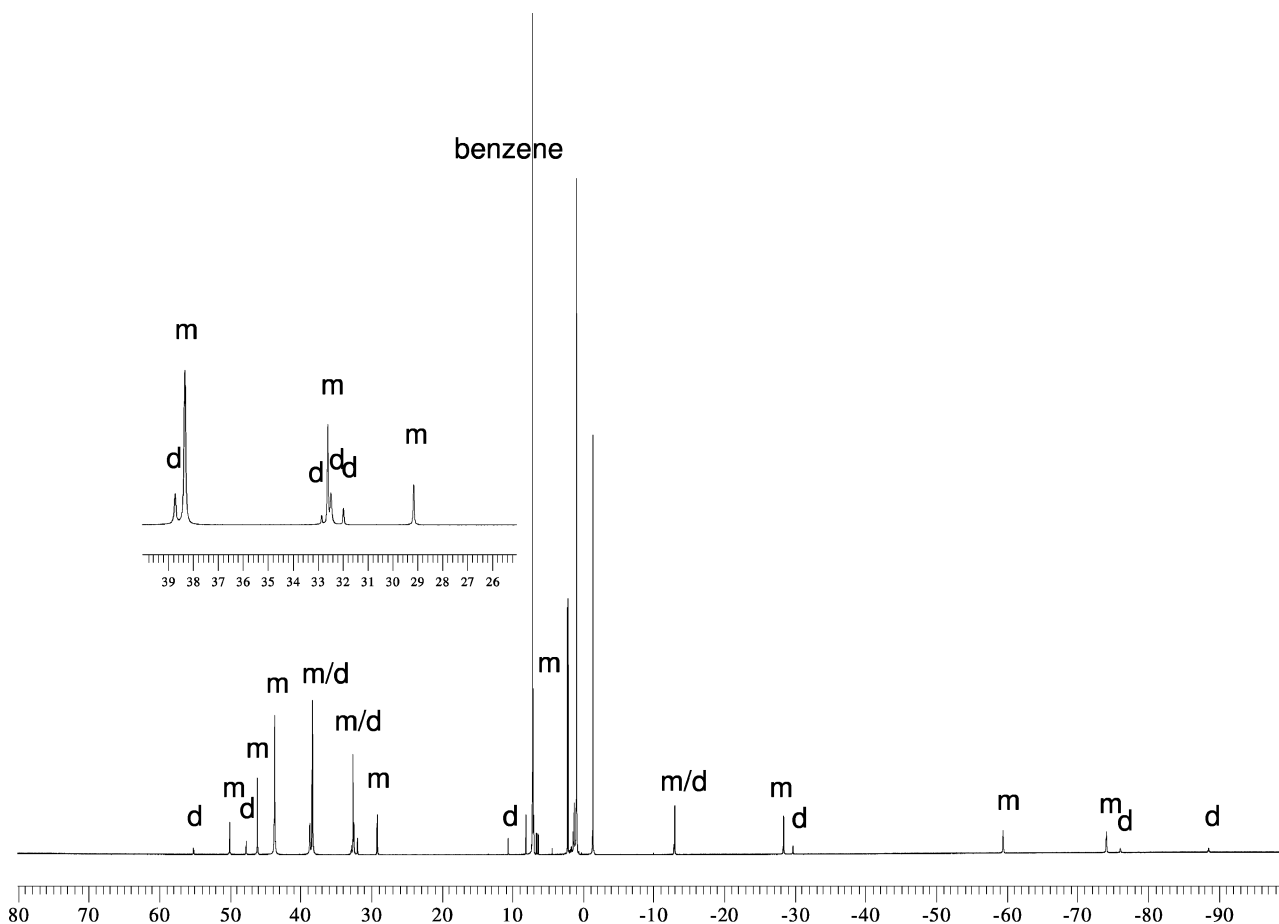
$+13.68\text{kJ/mol}$  and  $\Delta S = 40.32\text{ J/(mol K)}$  for **1** and  $\Delta H = +8.35\text{ kJ/mol}$  and  $\Delta S = 15.21\text{ J/(mol K)}$  for **3**, respectively. As observed with other transition-metal dimer/monomer equilibria, the equilibrium is enthalpically disfavored but entropically favored.<sup>7d</sup> In comparison with the monomer/dimer equilibrium reported for  $\beta$ -diketiminato nickel halide complexes,<sup>7c</sup> the equilibrium for the anilido–imino nickel complexes in solution showed smaller  $\Delta H$  values, which suggests that anilido–imino nickel complexes have a smaller tendency to dimerize than do  $\beta$ -diketiminato nickel halide complexes. In addition, the  $\Delta H$  value of complex **1** in solution is larger than that of complex **3**. It seems that the greater steric effect of complex **3** would make the equilibrium shift to a monomer.

**Olefin Polymerization.** Preliminary experiments indicated that no solid polymer was obtained, while complexes **1–4** catalyzed ethylene polymerization in the presence of MAO at atmospheric pressure or 10 atm pressure of ethylene. It is noteworthy that a small amount of oligomeric products were formed. GC-MS analysis (see the Supporting Information) confirmed that oligomers mainly contained dimers (butene) and trimers (hexene), and only traces of tetramers and higher oligomers were detected, which is a result of rapid  $\beta$ -H elimination in the process of the ethylene polymerization.

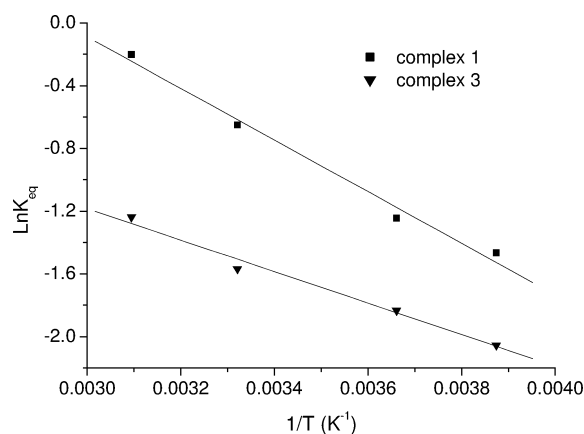
However, the anilido–imino nickel complexes showed high catalytic activities for norbornene polymerization after activation with MAO. The results of norbornene polymerizations using complexes **1–4** activated with MAO are summarized in Table 4. In general, the steric structure of the nickel complexes slightly influences their catalytic activities. The complex with bulky N-aryl groups exhibits higher catalytic activity. For example, at  $70^\circ\text{C}$ , complex **3** with two 2,6-diisopropyl N-aryl groups has the highest activity ( $4.60 \times 10^6\text{ g of PNBE/(mol of Ni h)}$ ) for norbornene polymerization, while complex **1** with two 2,6-dimethyl N-aryl groups has the lowest activity, which is in accord with the steric effect of the four complexes (**3** > **4**  $\approx$  **2** > **1**). However, the

(11) (a) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049. (b) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 2523. (c) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325.

(12) Institute of inorganic chemistry of Tianjian University. *Inorganic Chemistry*; Academic Press: Beijing, 1994; p 30.



**Figure 5.**  $^1\text{H}$  NMR spectrum of complex **1** in 35 mM benzene- $d_6$  solution at 18 °C using benzene- $d_6$  (7.15 ppm) as internal standard. The ratio of integration (m/d) is  $\sim 5:1$ , where m refers to the monomer and d refers to the dimer.



**Figure 6.** van't Hoff plots of complex **1** (45 mM) and complex **3** (25 mM) in toluene- $d_8$ .

steric structure of the nickel complexes does not practically influence the molecular weight of the produced polymer.

It is necessary to use an excessive amount of MAO for good to high activities. With an increased ratio of Al/Ni of 5800, the catalytic activity increased significantly up to  $6.8 \times 10^6$  g of PNBE/(mol of Ni) h). In contrast, the molecular weights ( $M_w$ ) of the polymers decreased with an increasing Al/Ni ratio. This result can be ascribed to the chain transfer to  $\text{AlMe}_3$  which is usually contained in MAO.<sup>13</sup>

**Table 4. Norbornene Polymerization with Anilido–Imino Nickel Complexes 1–4/MAO<sup>a</sup>**

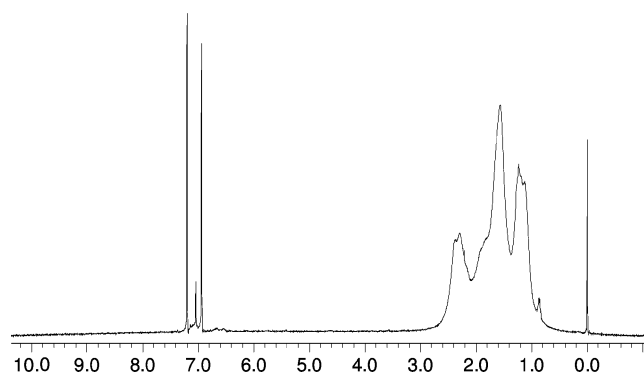
entry	complex	Al/Ni <sup>b</sup>	yield (%)	activity <sup>c</sup>	$M_w^d$	$M_w/M_n$
1	<b>1</b>	3000	39.5	3.16	1.21	2.25
2	<b>2</b>	3000	48.5	3.88	1.38	3.17
3	<b>3</b>	3000	57.5	4.60	1.39	2.90
4	<b>4</b>	3000	55.9	4.47	1.37	2.49
5	<b>3</b>	0	0	0		
6	<b>3</b>	1200	12.3	0.98	1.60	2.53
7	<b>3</b>	2100	39.0	3.12	1.51	2.64
8	<b>3</b>	5800	84.5	6.76	1.18	3.20

<sup>a</sup> Polymerization conditions: polymerization temperature 70 °C; polymerization time 0.5 h; nickel complex 1  $\mu\text{mol}$ ; monomer concentration [NBE] = 0.2 g/mL, solvent toluene, total volume 20 mL. <sup>b</sup> In units of mol/mol. <sup>c</sup> In units of  $10^{-6}$  g of PNBE/(mol of Ni) h). <sup>d</sup> In units of  $10^{-6}$  g/mol. Molecular weights were determined by GPC, and calibration was carried out with polystyrene standards.

The IR spectra of the obtained polymer reveal no traces of double bonds that often appear at 1620–1680, 735, and 966  $\text{cm}^{-1}$ <sup>14a</sup> (see the Supporting Information), and the  $^1\text{H}$  NMR spectra (Figure 7) also supply the same information.<sup>14b</sup> This ensures the occurrence of vinyl-type polymerization rather than ring-opening metathesis polymerization (ROMP).<sup>3g</sup> TGA curves of all the obtained polymers show that all of the polymer samples were very stable up to 450 °C. All polymers are soluble

(14) (a) IR (KBr,  $\text{cm}^{-1}$ ): 2945.91 (vs), 2867.38 (vs), 1474.12 (s), 1452.82 (s), 1375.19 (m), 1294.28 (m), 1257.47 (m), 1222.05 (m), 1189.09 (m), 1146.26 (m), 1107.66 (m), 1040.52 (w), 940.94 (m), 891.32 (m). (b)  $^1\text{H}$  NMR (500 MHz, *o*-dichlorobenzene- $d_4$ , room temperature, TMS as internal standard): 0.831, 0.847, 0.858, 0.870, 1.125, 1.238, 1.561, 2.214, 2.293.

(13) Wu, Q.; Gao, Q.; Lin, S. *J. Appl. Polym. Sci.* **1998**, *70*, 765.



**Figure 7.**  $^1\text{H}$  NMR spectrum of polynorbornene prepared from **3**/MAO at 70 °C.

in chlorobenzene, *o*-dichlorobenzene, and cyclohexane at room temperature, which indicates a low stereoregularity.

### Conclusion

Anilido–imino nickel complexes exist in the form of dinuclear bromine-bridged structures with tetrahedral geometries about nickel in the solid state. Due to the unbalanced steric effects of the *N*-aryl groups, there is a more crowded steric environment of the nickel atom for **2** than for **4**, even though these two complexes have the same composition. However, there is an equilibrium that shifts between the monomer and dimer depending on solvent, concentration, and temperature. Equilibrium constants and thermodynamic parameters ( $\Delta H$ ,  $\Delta S$ ) are consistent with the proposed equilibria. Complex **1** with both 2,6-dimethyl substituted aryls has a greater tendency to dimerize in solution than complex **3** with both 2,6-diisopropyl substituted aryls under the same conditions, which can be attributed to the steric effects of aryl groups. The anilido–imino nickel complexes show low activities for ethylene oligomerization but high activities up to  $6.80 \times 10^6$  g of PNBE/(mol of Ni) h for norbornene polymerization after activation with MAO. The steric effect slightly influenced their catalytic activities. The obtained homopolymers are vinyl-addition polynorbornene and show low stereoregularity.

### Experimental Section

**General Considerations.** All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk and vacuum-line techniques. Toluene, hexane, and THF were dried over sodium metal and distilled under nitrogen; benzene-*d*<sub>6</sub> and toluene-*d*<sub>8</sub> (Aldrich) were dried over CaH<sub>2</sub>. 2-Fluorobenzaldehyde (97%), 1,2-dimethoxyethane (99%), anhydrous nickel(II) bromide (99%), 2,6-diisopropylaniline (90%), and 2,6-dimethylaniline were bought from Aldrich Chemical Co. and used without further purification. The *n*-butyllithium solution in hexane (2.6 M) was purchased from Aldrich. Norbornene (bicyclo[2.2.1]hept-2-ene; Acros) was purified by distillation over potassium and used as a solution (0.4 g/mL) in toluene. (DME)NiBr<sub>2</sub> was synthesized by the reaction of 1,2-dimethoxyethane with anhydrous nickel(II) bromide, according to the report in the literature.<sup>15</sup> Methylaluminoxane (MAO) was prepared by partial hydrolysis of trimethylaluminum (TMA) in toluene at 0–60 °C with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O as

the water source. The initial [H<sub>2</sub>O]/[TMA] molar ratio was 1.3. Other commercially available reagents were purchased and used without purification.

**Measurement.** Elemental analyses were performed on a Vario EL microanalyzer. Mass spectra were measured on a LC/MS instrument using electrospray ionization (EI). NMR spectra were carried out on an INOVA 500 Hz instrument at room temperature in CDCl<sub>3</sub> solution for ligands, C<sub>6</sub>D<sub>6</sub> and C<sub>7</sub>D<sub>8</sub> solutions for complexes, and *o*-dichlorobenzene solution for polymers (using solvent as the internal standard for  $^1\text{H}$  NMR). IR spectra were recorded on a Nicolet NEXUS-670 FT-IR spectrometer. UV–vis spectra were measured on a UV-2450 spectrophotometer. Analysis of ethylene oligomers was performed by GC-MS on a Voyager GC-8000 TOP gas chromatograph–mass spectrometer. The following temperature program of the oven was adopted: 40 °C for 5 min, the temperature was increased by 8 °C/min heating to 110 °C, and then the temperature was increased by a 15 °C/min heating until 180 °C was reached; this value was kept constant for a further 5 min. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution of the polymers were performed on a Waters 150C instrument using standard polystyrene as the reference and with chlorobenzene as the eluent at 40 °C. TGA data were measured with a TG-290C thermal analysis system instrument.

**Syntheses of Ligands. *o*-C<sub>6</sub>H<sub>4</sub>F(CH=NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6).** A solution of 11.68 g of *o*-fluorobenzaldehyde (10 mL, 94.21 mmol) and 10.38 g of 2,6-diisopropylaniline (10.55 mL, 85.65 mmol) in *n*-hexane (40 mL) was stirred for 2 h before MgSO<sub>4</sub> was added. The mixture was then filtered, and the bright yellow solution was evaporated to dryness in vacuo to give a yellow oil. The oil was distilled under reduced pressure, and a light yellow distillate at 162–163 °C/5 mmHg was collected. Yield: 14.34 g (73.7%). EI-MS (*m/z*): 228.2 [M]<sup>+</sup>.  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>): 8.529(s, 1H, CH=NAr), 8.238 (dt, 7 Hz, 2 Hz, 1H, Ph), 7.441(q, *J* = 7.5 Hz, 1H, Ph), 7.223 (t, *J* = 8.0 Hz, 1H, Ph), 7.112–7.036 (m, 3H, Ph), 6.32 (t, *J* = 7.5 Hz, 1H, Ph), 2.144 (s, 6H, CH<sub>3</sub>).  $^{13}\text{C}$  NMR (125 Hz, CDCl<sub>3</sub>): 163.793 (d, *J* = 252 Hz, CF), 156.099, 151.208, 132.917, 128.048, 127.569, 126.896, 124.401, 123.836, 115.927, 18.187. Anal. Calcd for C<sub>15</sub>H<sub>14</sub>FN: C, 79.22; H, 6.27; N, 6.16. Found: C, 79.07; H, 6.21; N, 6.01.

***o*-C<sub>6</sub>H<sub>4</sub>{NH(C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6)}(CH=NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6) (L1).** Ligand **L1** was prepared by a similar method reported previously.<sup>9</sup> A 9.9 mL portion of an *n*-butyllithium solution in hexane (2.6 M) was added to a solution of 2,6-dimethylaniline (3.3 mL) in THF (30 mL) at –78 °C, and the mixture was warmed to room temperature overnight. The resulting solution of LiNHAr was cannula-transferred into a solution of *o*-C<sub>6</sub>H<sub>4</sub>F(CH=NC<sub>6</sub>H<sub>3</sub>Me-2,6) (5 mL) in 30 mL of THF at 25 °C. After the reaction mixture was stirred for 1 h, it was quenched with 15 mL of H<sub>2</sub>O, extracted with *n*-hexane, and evaporated to dryness in vacuo. The resulting yellow oil was dissolved in hot methanol (~500 mL) and then cooled slowly to –10 °C to give 3.18 g of pale yellow crystals that were dried in vacuo. Yield: 41.3%. EI-MS (*m/z*): 329.2 [M]<sup>+</sup>.  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>): 10.495 (s, 1H, NH), 8.367 (s, 1H, CH=NAr), 7.345 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H, Ph), 7.182–7.077 (m, 6H, Ph), 6.961 (t, *J* = 7.5 Hz, 1H, Ph), 6.285 (d, *J* = 8.5 Hz, 1H, Ph), 2.241 (s, 6H, CH<sub>3</sub>), 2.190 (s, 6H, CH<sub>3</sub>).  $^{13}\text{C}$  NMR (125 Hz, CDCl<sub>3</sub>): 165.932, 150.777, 148.464, 137.475, 136.747, 134.527, 132.192, 128.352, 128.092, 127.638, 126.370, 123.783, 116.706, 115.344, 111.756, 18.500. Anal. Calcd for C<sub>23</sub>H<sub>24</sub>N<sub>2</sub>: C, 84.04; H, 7.43; N, 8.52. Found: C, 84.24; H, 7.51; N, 8.52.

***o*-C<sub>6</sub>H<sub>4</sub>{NH(C<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub>-2,6)}(CH=NC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>-2,6) (L2).** The synthesis of ligand **L2** was carried out as described for ligand **L1**. A 5.0 mL portion of *o*-C<sub>6</sub>H<sub>4</sub>F(CH=NC<sub>6</sub>H<sub>3</sub>Me-2,6), 5.1 mL of 2,6-diisopropylaniline, and 9.9 mL of *n*-butyllithium (2.6 M) were converted to **L2**, and 3.99 g of pale yellow crystals was obtained. Yield: 44.4%. EI-MS (*m/z*): 385.2 [M]<sup>+</sup>.  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>): 10.515 (s, 1H, NH), 8.371 (s, 1H, CHNAr),

(15) Hart, W. X. Doctoral Dissertation, University of Massachusetts, 1981.

7.340–7.292 (m, 2H, Ph), 7.246–7.243 (m, 2H, Ph), 7.147 (dt,  $J = 8.5$  Hz, 1.5 Hz, 1H, Ph), 7.090 (d,  $J = 8.0$  Hz, 2H, Ph), 6.960 (t,  $J = 7.5$  Hz, 1H, Ph), 6.689 (dt,  $J = 7.5$  Hz, 1 Hz, 1H, Ph), 6.289 (d,  $J = 7.5$  Hz, 1H, Ph), 3.201 (sp,  $J = 7.0$  Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 2.185 (s, 6H,  $\text{CH}_3$ ), 1.151 (d,  $J = 6.0$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (125 Hz,  $\text{CDCl}_3$ ): 166.018, 150.879, 149.941, 147.489, 134.621, 134.441, 132.178, 128.070, 127.638, 127.472, 123.761, 116.296, 115.114, 112.022, 28.545, 24.704, 22.982, 18.385. Anal. Calcd for  $\text{C}_{27}\text{H}_{32}\text{N}_2$ : C, 84.26; H, 8.46; N, 7.28. Found: C, 84.21; H, 8.48; N, 7.06.

**$o\text{-C}_6\text{H}_4\text{F}(\text{CH}=\text{NC}_6\text{H}_3\text{Pr}_2\text{-2,6})$ .** The synthesis was carried out as described for  $o\text{-C}_6\text{H}_4\text{F}(\text{CH}=\text{NC}_6\text{H}_3\text{Me}_2\text{-2,6})$ , but 2,6-diisopropylaniline was used in place of 2,6-dimethylaniline. A mixture of 11.5 g of  $o$ -fluorobenzaldehyde (9.85 mL, 92.8 mmol) and 18.1 g of 2,6-diisopropylaniline (19.25 mL, 102 mmol) in  $n$ -hexane (40 mL) was stirred for 2 h before  $\text{MgSO}_4$  was added. The mixture was then filtered; the bright yellow solution was cooled to  $-10$  °C to give 13.46 g of large yellow blocklike crystals. The filtrate was condensed to lower volume and cooled to  $-10$  °C to give an additional 4.3 g of pure crystals. Total yield: 17.76 g (68%). EI-MS ( $m/z$ ): 284.3  $[\text{M}]^+$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 8.509 (s, 1H,  $\text{CH}=\text{NAr}$ ), 8.224 (dt,  $J = 7.5$  Hz, 2.0 Hz, 1H, Ph), 7.481 (q,  $J = 7.5$  Hz, 1H, Ph), 7.273 (t,  $J = 7.5$  Hz, 1H, Ph), 7.241–7.084 (m, 4H, Ph), 2.957 (sp,  $J = 7.0$  Hz, 2H,  $\text{CHMe}_2$ ), 1.185 (d,  $J = 6.5$  Hz, 12H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR (125 Hz,  $\text{CDCl}_3$ ): 163.865 (d,  $J = 252$  Hz, CF), 155.670, 149.306, 137.558, 132.989, 127.754, 124.565, 124.329, 123.814, 123.057, 116.056, 27.955, 23.464. Anal. Calcd for  $\text{C}_{19}\text{H}_{22}\text{NF}$ : C, 80.53; H, 7.83; N, 4.94. Found: C, 80.37; H, 7.54; N, 4.73.

**$o\text{-C}_6\text{H}_4\{\text{NH}(\text{C}_6\text{H}_3\text{Pr}_2\text{-2,6})\}(\text{CH}=\text{NC}_6\text{H}_3\text{Pr}_2\text{-2,6})$  (L3).** The synthesis of ligand L3 has been reported,<sup>9</sup> which was carried out as described for ligand L1. A 10 g portion of  $o\text{-C}_6\text{H}_4\text{F}(\text{CH}=\text{NC}_6\text{H}_3\text{Pr}_2\text{-2,6})$ , 7.65 mL of 2,6-diisopropylaniline, and 14.8 mL of  $n$ -butyllithium (2.6 M) were converted to L3. A 6.3 g amount of pale yellow small crystals were obtained. Yield: 41%. EI-MS ( $m/z$ ): 441.4  $[\text{M}]^+$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 10.497 (s, 1H, NH), 8.353 (s, 1H,  $\text{CH}=\text{NR}$ ), 7.348 (dd,  $J = 7.5$ , 1.5 Hz, 1H, Ph), 7.319–7.288 (m, 1H, Ph), 7.242–7.222 (m, 3H, Ph), 7.169–7.091 (m, 4H, Ph), 6.693 (dt,  $J = 8$  Hz, 1.1 Hz, 1H, Ph), 6.289 (d,  $J = 8.5$  Hz, 1H, Ph), 3.215, 3.109 (sp,  $J = 7.0$  Hz, 2  $\times$  2H,  $\text{CHMe}_2$ ), 1.183 (d,  $J = 6.5$  Hz, 12H,  $\text{CHMe}_2$ ), 1.154, 1.140 (d,  $J = 5.5$  Hz, 12H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR (125 Hz,  $\text{CDCl}_3$ ): 165.810, 149.978, 148.684, 147.526, 138.223, 134.533, 134.476, 132.224, 127.504, 124.372, 123.800, 123.049, 116.192, 115.177, 112.030, 28.569, 28.076, 24.580, 23.543, 23.085. Anal. Calcd for  $\text{C}_{31}\text{H}_{40}\text{N}_2$ : C, 84.49; H, 9.15; N, 6.36. Found: C, 84.45; H, 9.43; N, 6.11.

**$o\text{-C}_6\text{H}_4\{\text{NH}(\text{C}_6\text{H}_3\text{Me}_2\text{-2,6})\}(\text{CH}=\text{NC}_6\text{H}_3\text{Pr}_2\text{-2,6})$  (L4).** The synthesis of ligand L4 was carried out as described for ligand L1. A 4.4 g portion of  $o\text{-C}_6\text{H}_4\text{F}(\text{CH}=\text{NC}_6\text{H}_3\text{Pr}_2\text{-2,6})$ , 2.2 mL of 2,6-dimethylaniline, and 6.5 mL of  $n$ -butyllithium (2.6 M) were converted to ligand L4; 2.82 g of pale yellow crystals was obtained. Yield: 47.2%. EI-MS ( $m/z$ ): 385.2  $[\text{M}]^+$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 10.556 (s, 1H, NH), 8.351 (s, 1H,  $\text{CH}=\text{NAr}$ ), 7.349 (dd,  $J = 7.5$  Hz, 1.5 Hz, 1H, Ph), 7.215–7.085 (m, 7H, Ph), 6.705 (dt,  $J = 8.0$  Hz, 1.0 Hz, 1H, Ph), 6.278 (d,  $J = 8$  Hz, 1H, Ph), 3.092 (sp,  $J = 7$  Hz, 2H,  $\text{CHMe}_2$ ), 2.210 (s, 6H,  $\text{CH}_3$ ), 1.186 (d,  $J = 7$  Hz, 12H,  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (125 Hz,  $\text{CDCl}_3$ ): 165.667, 148.734, 148.577, 138.058, 137.048, 136.900, 134.619, 132.259, 128.398, 128.467, 124.329, 123.028, 116.614, 115.377, 111.701, 28.112, 23.450, 18.237. Anal. Calcd for  $\text{C}_{27}\text{H}_{32}\text{N}_2$ : C, 84.26; H, 8.26; N, 7.28. Found: C, 84.34; H, 8.47; N, 7.11.

**Syntheses of Complexes.** Ligands were dissolved in 40 mL of toluene in a flame-dried Schlenk flask, and an  $n$ -butyllithium solution (2.6 M) was injected in a  $-78$  °C dry ice/acetone bath, which was warmed to room temperature overnight.  $(\text{DME})\text{NiBr}_2$  was added and then stirred for 24 h at 80 °C; the crude reaction mixture was followed by hot filtration under nitrogen. The dark green solution was evaporated to

low volume in vacuo, and then  $n$ -hexane (20:1) was added. Solvent was removed from the precipitate via cannula filtration, and the residual black green solid was washed with  $n$ -hexane ( $3 \times 5$  mL). Drying in vacuo produces the desired nickel complex. The nickel complex was dissolved in hot hexane/toluene (15:1) solution and cooled in a freezer several days to afford the product as dark green crystals.

**$[\text{Ni}(\text{2-C}_6\text{H}_4\{\text{N}(\text{C}_6\text{H}_3\text{Me}_2\text{-2,6})\}(\text{CH}=\text{NC}_6\text{H}_3\text{Me}_2\text{-2,6}))\text{Br}]_2$  (1).** The general procedure was employed with 1.10 g of ligand L1, 1.3 mL of  $n$ -butyllithium solution (2.6 M) and 1.04 g of  $(\text{DME})\text{-NiBr}_2$  to afford 1.22 g (77.9%) of the desired complex as a dark green solid. EI-MS ( $m/z$ ): 465, 466, 467, 468, 469, 470 (isotope,  $[\text{M}]^+$ ); 383, 384, 385, 386, 387 (isotope,  $[\text{M} - \text{Br}]^+$ ); 329 (ligand<sup>+</sup>).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz, 18 °C): 55.134 (0.2H,  $\text{CH}=\text{N}$ ), 49.996 (1H,  $\text{CH}=\text{N}$ ), 47.672 (0.4H, Ph), 46.091 (2H, Ph), 43.632 (6H,  $\text{CH}_3$ ), 38.680 (1.2H,  $\text{CH}_3$ ), 38.268 (6H,  $\text{CH}_3$ ), 32.810 (0.2H, Ph), 32.557 (2H, Ph), 32.433 (1.2H,  $\text{CH}_3$ ), 31.929 (0.4H, Ph), 29.115 (1H, Ph), 10.574 (0.2H, Ph), 7.015 (1H, Ph),  $-12.902$  (0.2H, backbone benzene),  $-13.002$  (1H, backbone benzene),  $-28.397$  (1H, backbone benzene),  $-29.728$  (0.2H, backbone benzene),  $-59.472$  (1H, backbone benzene),  $-74.096$  (1H, backbone benzene),  $-76.055$  (0.2H, backbone benzene),  $-86.565$  (0.2H, backbone benzene). In benzene- $d_6$ , monomer and dimer were observed in a  $\sim 10:1$  ratio on the basis of integration.  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ , 500 MHz, 28 °C): 58.974 (0.15H,  $\text{CH}=\text{N}$ ), 53.174 (1H,  $\text{CH}=\text{N}$ ), 51.037 (0.3H, Ph), 49.215 (2H, Ph), 47.105 (6H,  $\text{CH}_3$ ), 41.475 (6H + 0.9H,  $\text{CH}_3$ , overlap), 34.932 (0.9H,  $\text{CH}_3$ ), 34.768 (0.15H, Ph), 34.698 (2H, Ph), 34.021 (0.3H, Ph), 30.486 (1H, Ph), 10.569 (0.15H, Ph), 7.010 (1H, Ph),  $-14.599$  (1H + 0.15H, backbone benzene),  $-31.118$  (1H, backbone benzene),  $-32.679$  (0.15H, backbone benzene),  $-64.951$  (1H, backbone benzene),  $-81.089$  (1H, backbone benzene),  $-83.183$  (0.15H, backbone benzene),  $-96.982$  (0.15H, backbone benzene). The ratio of monomer and dimer is  $\sim 40:3$ . Anal. Calcd for  $\text{C}_{46}\text{H}_{46}\text{N}_4\text{Ni}_2\text{Br}_2$ : C, 59.00; H, 4.97; N, 6.01. Found: C, 58.53; H, 5.14; N, 6.19.

**$[\text{Ni}(\text{2-C}_6\text{H}_4\{\text{N}(\text{C}_6\text{H}_3\text{Pr}_2\text{-2,6})\}(\text{CH}=\text{NC}_6\text{H}_3\text{Me}_2\text{-2,6}))\text{Br}]_2$  (2).** The general procedure was employed with 1.21 g of ligand L2, 1.7 mL of  $n$ -butyllithium (2.6 M), and 1.35 g of  $(\text{DME})\text{NiBr}_2$  to afford 1.51 g (66.0%) of the desired complex as a dark green solid. EI-MS ( $m/z$ ): 521, 522, 523, 524, 525, 526 (isotope,  $[\text{M}]^+$ ); 439, 440, 441, 442, 443 (isotope,  $[\text{M} - \text{Br}]^+$ ); 385 (ligand<sup>+</sup>).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz, 18 °C): 56.854 (1H,  $\text{CH}=\text{N}$ ), 51.446 (0.3H,  $\text{CH}=\text{N}$ ), 49.697 (2H, Ph), 47.194 (0.6H, Ph), 41.375 (2H + 0.3H, Ph, overlap), 34.981 (1.8H,  $\text{CH}_3$ ), 34.405 (6H + 0.6H,  $2\text{CH}_3 + 2\text{H}$ , overlap), 33.736 (2H, Ph), 31.255 (0.3H, Ph), 19.311 (0.6H,  $\text{CH}(\text{CH}_3)_2$ ), 16.833 (2H,  $\text{CH}(\text{CH}_3)_2$ ), 8.362 (6H,  $\text{CH}(\text{CH}_3)_2$ ), 7.409 (1.8H,  $\text{CH}(\text{CH}_3)_2$ ), 4.613 (1.8H,  $\text{CH}(\text{CH}_3)_2$ ), 3.978 (6H,  $\text{CH}(\text{CH}_3)_2$ ),  $-13.454$  (1H, backbone benzene),  $-15.015$  (0.30H, backbone benzene),  $-27.803$  (0.30H, backbone benzene),  $-32.271$  (1H, backbone benzene),  $-64.329$  (0.30H, backbone benzene),  $-79.472$  (0.30H, backbone benzene),  $-96.295$  (1H, backbone benzene). The ratio of monomer and dimer is  $\sim 20:3$ . Anal. Calcd for  $\text{C}_{54}\text{H}_{62}\text{N}_4\text{Ni}_2\text{Br}_2$ : C, 62.10; H, 5.99; N, 5.36. Found: C, 61.52; H, 6.08; N, 5.01.

**$[\text{Ni}(\text{2-C}_6\text{H}_4\{\text{N}(\text{C}_6\text{H}_3\text{Pr}_2\text{-2,6})\}(\text{CH}=\text{NC}_6\text{H}_3\text{Pr}_2\text{-2,6}))\text{Br}]_2$  (3).** The general procedure was employed with 1.14 g of ligand L3, 1.0 mL of  $n$ -butyllithium (2.6 M), and 0.795 g of  $(\text{DME})\text{NiBr}_2$  to afford 0.67 g (45.0%) of the desired complex as a dark green solid. EI-MS ( $m/z$ ): 577, 579, 580, 581, 582, 583 (isotope,  $\text{M}^+$ ); 495, 496, 497, 498, 499 (isotope,  $[\text{M} - \text{Br}]^+$ ); 441 (ligand<sup>+</sup>).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz, 18 °C): 53.367 (0.16H,  $\text{CH}=\text{N}$ ), 47.470 (1H,  $\text{CH}=\text{N}$ ), 45.904 (0.32H, Ph), 43.129 (2H, Ph), 33.164 (0.16H, Ph), 31.574 (2H + 0.32H, Ph, overlap), 29.116 (1H, Ph), 26.560 (2H,  $\text{CH}(\text{CH}_3)_2$ ), 20.736 (0.32H, Ph), 18.079 (2H,  $\text{CH}(\text{CH}_3)_2$ ), 15.461 (0.32H,  $\text{CH}(\text{CH}_3)_2$ ), 10.772 (0.16H, Ph), 8.245 (1H, Ph), 7.271–5.926 (18H + 2.88H,  $\text{CH}_3$ ), 4.349–4.199 (6.96H,  $\text{CH}_3$ ),  $-11.620$  (1.16H, backbone benzene, overlap),  $-24.796$  (1H, backbone benzene),  $-26.954$  (0.16H, backbone benzene),  $-56.986$  (1H, backbone benzene),  $-69.933$  (1H, backbone benzene),  $-75.320$  (0.16H, backbone benzene),

–88.030 (0.16H, backbone benzene). The ratio of monomer and dimer is ~12.5:1.  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ , 500 MHz, 28 °C): 57.146 (0.2H, CH=N), 50.838 (1H, CH=N), 49.146 (0.4H, Ph), 46.243 (2H, Ph), 35.404 (0.2H, Ph), 33.711 (2H + 0.4H, Ph, overlap), 33.218 (0.4H, Ph), 30.830 (1H, Ph), 28.574 (2H,  $\text{CH}(\text{CH}_3)_2$ ), 21.862 (0.4H,  $\text{CH}(\text{CH}_3)_2$ ), 19.074 (2H,  $\text{CH}(\text{CH}_3)_2$ ), 16.421 (0.4H,  $\text{CH}(\text{CH}_3)_2$ ), 10.772 (0.2H, Ph), 9.162 (1H, Ph), 7.239–6.321 (18H + 3.6H,  $\text{CH}_3$ ), 4.408 (6H + 1.2H,  $\text{CH}_3$ ), –12.526 (0.2H, backbone benzene), –13.228 (1H, backbone benzene), –27.471 (1H, backbone benzene), –29.900 (0.2H, backbone benzene), –62.745 (1H, backbone benzene), –77.233 (1H, backbone benzene), –82.241 (0.2H, backbone benzene), –96.143 (0.2H, backbone benzene). The ratio of monomer and dimer is ~10:1. Anal. Calcd for  $\text{C}_{62}\text{H}_{78}\text{N}_4\text{Ni}_2\text{Br}_2$ : C, 64.39; H, 6.80; N, 4.84. Found: C, 63.68; H, 7.01; N, 4.62.

**[Ni(2- $\text{C}_6\text{H}_4\{\text{N}(\text{C}_6\text{H}_3\text{Pr}_2\text{-2,6})\}(\text{CH}=\text{NC}_6\text{H}_3\text{Me-2,6})\text{Br}_2$ )]<sub>2</sub> (4).** The general procedure was employed with 1.27 g of ligand **L4**, 1.3 mL of *n*-butyllithium (2.6 M), and 1.02 g of (DME)NiBr<sub>2</sub> to afford 0.98 g (56.9%) of the desired complex as a dark green solid. EI-MS (*m/z*): 521, 522, 523, 524, 525, 526 (isotope, [M]<sup>+</sup>); 439, 440, 441, 442, 443 (isotope, [M – Br]<sup>+</sup>); 385 (ligand<sup>+</sup>).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz, 18 °C, saturated solution): 57.494 (1H, CH=N), 52.101 (0.8H, CH=N), 48.542 (2H, Ph), 48.180 (1.6H, Ph), 45.792 (4.8H,  $\text{CH}_3$ ), 38.963 (6H,  $\text{CH}_3$ ), 34.214 (2H, Ph), 33.672 (2H, Ph), 29.802 (1.6H, Ph), 28.776 (1.6H, Ph), 23.575 (2H + 1.6H,  $\text{CH}(\text{CH}_3)_2$ , overlap), 7.980 (6H,  $\text{CH}(\text{CH}_3)_2$ ), 6.615 (4.8H,  $\text{CH}(\text{CH}_3)_2$ ), 6.302 (4.8H,  $\text{CH}(\text{CH}_3)_2$ ), 5.270 (6H,  $\text{CH}(\text{CH}_3)_2$ ), –12.133 (0.8H, backbone benzene), –13.230 (1H, backbone benzene), –30.067 (0.8H, backbone benzene), –31.287 (1H, backbone benzene), –62.696 (0.8H, backbone benzene), –78.229 (0.8H, backbone benzene), –81.565 (1H, backbone benzene), –92.919 (1H, backbone benzene). The ratio of monomer and dimer is ~5:2 in saturated benzene solution. Anal. Calcd for  $\text{C}_{54}\text{H}_{62}\text{N}_4\text{Ni}_2\text{Br}_2$ : C, 62.10; H, 5.99; N, 5.36. Found: C, 61.45; H, 6.17; N, 5.01.

**Ethylene Polymerization.** A 50 mL stainless steel autoclave was charged with 25 mL of a toluene solution of MAO under 1 atm of ethylene at initialization temperature. The system was maintained by continuously stirring for 30 min, and then 5 mL of the nickel complex solution (5 mM) was charged into the autoclave under 1 atm of ethylene. The ethylene pressure was raised to the specified value, and the reaction was carried out for a certain time. Polymerizations were terminated by addition of ethanol after releasing ethylene pressure.

**Norbornene Polymerization.** In a typical procedure, the appropriate methylaluminoxane (MAO) solid was introduced into the round-bottom glass flask, and then 10 mL of a toluene solution of norbornene (0.4 g/mL) was added via syringe. Toluene (14 mL) and 1 mL of the nickel complex solution (1 mM) were syringed into the well-stirred solution in order, and the reaction mixture was continuously stirred for an appropriate period at the polymerization temperature. Polymerizations were terminated by addition of 200 mL of the acidic ethanol (ethanol–HCl, 95:5). The resulting precipitated polymers were collected and treated by filtering, washing with ethanol several times, and drying under vacuum at 60 °C to a constant weight.

**Crystal Structure Determination.** The crystals were mounted on a glass fiber using the oil drop scan method.<sup>16</sup> Data obtained with the  $\omega$ – $2\theta$  scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293 K. The structures were solved using direct methods, while further refinement with full-matrix least squares on  $F^2$  was obtained with the SHELXTL program package.<sup>17,18</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

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**Supporting Information Available:** Tables and figures giving X-ray crystallographic details for **1**, **2**, and **4** as CIF files and figures giving GC-MS spectra of oligomers and FT-IR spectra of the polynorbornene in PDF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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