# ORGANOMETALLICS

# Synthesis of New Bis(amidine)–Cobalt Catalysts and Their **Application to Styrene Polymerization**

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S Supporting Information

ABSTRACT: Two new bis(amidine) cobalt(II) complexes were rationally designed and efficiently synthesized. The first synthesized cobalt complex was based on a cyclic bis(amidine) ligand with chiral vicinal diphenyl groups. The structure was verified by single-crystal X-ray crystallography. As expected from the ligand structure, the Co-N bonds in this complex were significantly shorter than those found in the corresponding 1,2-diimine cobalt complex. This indicates that the bis(amidine) ligand has better electron-donating capability than the 1,2-diimine ligand. Upon test polymerization of styrene, the complex exhibited a moderate activity of 5.88  $\times$ 



10<sup>5</sup> g PS/(mol Co h). On the basis of this encouraging result, a new 1,2-diaminobenzene-derived bis(amidine) ligand was efficiently synthesized and used to make the corresponding cobalt(II) complex. When subjected to styrene polymerization, the resulting complex showed unusually high polymerization activity  $[164 \times 10^5 \text{ g PS}/(\text{mol Co h})]$  and high conversion (>99%). The resulting polymer was identified as atactic polystyrene by <sup>13</sup>C NMR spectroscopy analysis. The significantly enhanced styrene polymerization activity of the 1,2-diaminobenzene-originated bis(amidine) cobalt(II) complex is attributed to the improved electron-donating capability of the ligand.

# INTRODUCTION

Since Ziegler-Natta-type catalysts were developed, the field of transition metal catalyzed olefin polymerization has continued to grow worldwide in both industry and academics.<sup>1</sup> Early on, the heterogeneous catalytic system evolved into homogeneous single-site catalytic systems focused on early transition metal metallocene complexes.<sup>2a,b</sup> The research paradigm then shifted to nonmetallocene late transition metal complexes after Brookhart and co-workers reported the stunning catalytic activity of new palladium(II)- and nickel(II)-based catalysts with  $\alpha$ -diimine ligands in 1995.<sup>3</sup> The beauty of their catalyst design lies in the easy synthesis and structural variation of bidentate  $\alpha$ -diimine ligands.<sup>4</sup> In general, the electron density of nitrogen atoms in  $\alpha$ -diimine ligands can be tuned by changing substituents on the N-aryl rings. However, variation of the Naryl groups in Brookhart-type catalysts may have little effect on the donacity of nitrogen chelating sites. This is because bulky N-aryl groups are orthogonal to  $\alpha$ -diimine groups, so there is minimal delocalization of the lone-pair electrons of nitrogens to the N-aryl groups.

We propose a new transition metal complex design based on bis(amidine) ligands in which the electron-donating ability of the ligand is enhanced compared to  $\alpha$ -diimine-derived catalysts. We also explored the catalytic activity of the new complexes in olefin polymerization. As shown in Figure 1, bis(amidine) has two exo-amino groups that could enhance the electron density of nitrogen when coordinated to metal. Bis(amidine) has the



Figure 1. Design of a new styrene polymerization catalyst based on a bis(amidine) ligand.

advantage of enhancing structural variation because various substituents can easily be introduced on the exo-amino groups. Despite their structural versatility, bis(amidine) ligand-based transition metal olefin polymerization catalysts have rarely been studied.<sup>5</sup>

In this paper, we report the synthesis of two new bis(amidine) cobalt(II) complexes (6, 12) and their unusually high activities in styrene polymerization.

# **RESULTS AND DISCUSSION**

Synthesis of Chiral Bis(amidine) Cobalt(II) Complex (6). Chiral bis(amidine) ligand 5 was initially designed and

Received: December 10, 2013

synthesized to develop a catalyst for asymmetric Kumada-type coupling reactions.<sup>6</sup> The synthesis of chiral cobalt complex **6** is described in Scheme 1. Commercially available 2-isopropyl

### Scheme 1. Synthesis of Chiral Bis(amidine) Cobalt(II) Complex 6



aniline (1) was reacted with a half an equivalent of oxalyl chloride in the presence of triethylamine to provide oxalamide 2 in 92% yield.<sup>7</sup> Treatment of oxalamide 2 with PCl<sub>5</sub> yielded oxalimidoyl dichloride 3. Oxalimidoyl dichloride 3 was then reacted with  $(1R,2R)-N^1,N^2$ -dimethyl-1,2-diphenylethane-1,2-diamine (4) to provide the desired chiral bis(amidine) 5.  $(1R,2R)-N^1,N^2$ -Dimethyl-1,2-diphenylethane-1,2-diamine (4) was prepared following the literature procedure.<sup>8</sup> Finally, refluxing the mixture of chiral bis(amidine) 5 and CoCl<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> provided the desired cobalt(II) complex 6 as sky blue crystals [mp: decomposed at 315 °C].

X-ray Structure of 6. Single crystals of 6 suitable for X-ray crystallography were obtained from CH<sub>2</sub>Cl<sub>2</sub> solution by slow evaporation. The molecular structure determined by singlecrystal X-ray diffraction is shown in Figure 2 as an ORTEP drawing. Selected bond lengths and angles are listed in Table 1 along with analogous structural data extracted from Rosa's 1,2diimine cobalt catalyst  $A^9$  to verify the improved donating effect of the bis(amidine) ligand compared to that of the 1,2-diimine ligand. The Co1-N distances in 6 (2.025(3) and 2.013(3) Å) are significantly shorter than those in A (2.084(6) and 2.067(6))Å). Conversely, N1-C1 and N2-C2 bond lengths in 6 (1.301(5) and 1.298(5) Å) are longer than those of A (1.232(8) and 1.283(8) Å). These key structural features imply that the bis(amidine) ligand gives more electron density to the cobalt ion and is a better electron-donating ligand than 1,2diimine, as was envisioned. The cobalt bound to two amidine nitrogens adopts tetrahedral geometry with two chlorides. The Cl1-Co1-Cl2 angle is 116.00(5)°, while the N1-Co1-N2 bite angle is  $81.12(13)^\circ$ . The bond lengths of Co-Cl are



Figure 2. ORTEP drawing of 6 showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

2.2322(12) and 2.2386(12) Å, respectively, and the Co–N bond distances are 2.013(3) and 2.025(3) Å. It is noteworthy that the C1–N1–C12 angle (123.5(3)°) is significantly larger than the corresponding C–N–C angle (115°) in  $\alpha$ -diimine cobalt complex **A**.<sup>9</sup> This is mainly because the two 2-isopropylphenyl rings are pushed away due to the two N-methyl groups (C21 and C22). This implies that the two 2-isopropylphenyl groups on the amidine nitrogens in **6** may cause more shielding of the cobalt complex on the front side than the two 2,6-diisopropylphenyl rings in **A**. In addition, the two 2-isopropylphenyl rings on N1 and N2 are located perpendicular to the plane of Co1–N1–C1–C2–N2, while the two isopropyl groups are antiperiplanar to each other.

Styrene Polymerization with Catalyst 6. Since complex 6 was envisioned as a good catalyst for styrene polymerization, test polymerization was conducted using 6 as a catalyst and methylaluminoxane (MAO) as cocatalyst (Scheme 2). The reaction conditions were set following typical literature conditions.<sup>10a-d</sup> This catalyst exhibited a catalyst activity of  $5.88 \times 10^5$  g PS/(mol Co h), which is a reasonably high activity for the first trial.

Most reported styrene polymerization catalysts have been based on nickel complexes, while cobalt complexes are rarely investigated. For example, Wang and colleagues reported a pyrazolylimine nickel catalyst with an activity up to  $8.45 \times 10^5$  g PS/(mol Ni h).<sup>10a</sup> The Li group also reported styrene polymerization catalysts based on a  $\beta$ -diketiminate nickel(II) complex<sup>10b</sup> showing activity up to  $8.24 \times 10^5$  g PS/(mol Ni h). The Gomes group studied  $\alpha$ -diimine nickel(II) complexes for styrene polymerization that exhibited activity up to  $2.79 \times 10^5$  g PS/(mol Ni h).<sup>10c,d</sup> We also prepared a bis(amidine) nickel dichloride complex with ligand **5** (see Supporting Information), which is analogous to cobalt catalyst **6**, and tested its activity in styrene polymerization. However, this nickel-based catalyst did not show any styrene polymerization activity under the same conditions.

On the basis of these preliminary results, our attention quickly shifted to the catalytic polymerization activity of cobalt complex **6**. The new bis(amidine) cobalt complex **12**, an achiral version of **6**, was prepared as the polymerization catalyst, as shown in Scheme 3.

Table 1. Comparison of Selected Bond Lengths and Angles of Rosa's 1,2-Diimine Cobalt Complex A<sup>9</sup> and Chiral Bis(amidine) Cobalt(II) Complex 6



Synthesis of Achiral Bis(amidine) Cobalt(II) Complex (12). Since catalyst chirality is not essential for polymerization, the chiral 1,2-diphenyl-1,2-diaminoethylene moiety in 6 was replaced with achiral *o*-phenylenediamine. The bis(amidine) structure was maintained by adopting a quinoxaline fragment, and the synthetic scheme was devised so that synthesis was economical and efficient. Commercially available *o*-phenylenediamine (7) was reacted with a half an equivalent of oxalic acid in the presence of aqueous HCl to afford oxalamide 8 in 98% yield. Treatment of oxalamide 8 with SOCl<sub>2</sub> yielded 2,3-dichloroquinoxaline 9.<sup>11</sup> 2,3-Dichloroquinoxaline 9 was then reacted with 2-isopropylaniline (1) to afford the desired  $N^2$ , $N^3$ -bis(2-isopropylphenyl)quinoxaline-2,3-diamine (10). The de-









sired achiral bis(amidine) ligand 11 was prepared by methylation of compound 10 with iodomethane and sodium hydride in DMSO. Finally, refluxing a mixture of bis(amidine) 11 and CoCl<sub>2</sub> in EtOH yielded cobalt(II) complex 12 as a yellowish-green powder [mp: decomposed at 168 °C]. The desired cobalt complex 12 was obtained in 45% overall yield via five steps. This is significantly improved compared to the synthesis of a chiral cobalt complex with a more expensive chiral diamine (16% overall yield, four steps).

Styrene Polymerization with Catalyst 12. Styrene polymerization was attempted with the newly synthesized achiral cobalt complex 12 under various conditions. Reactions were initially carried out and monitored in an NMR tube. The reactions were very fast, with some completed in 10 min and most completed in less than 60 min (see Supporting Information). To screen catalytic activity, the reactions were performed in 3 g of styrene, and the catalyst concentration was fixed at 16  $\mu$ M. Toluene was chosen as a polymerization solvent, and the results are summarized in Table 2.

As a control experiment, polymerization was attempted without catalyst, but this attempt did not produce any polymer (entry 1). The use of cocatalyst (MAO) was critical because polymerization did not proceed without MAO even in the presence of catalyst **12** (entry 2). Since the presence of both

Table 2. Styrene Polymerization with Catalyst 12 or  $A^{a}$ 

		cat (16 μM) MAO, tol, 1 h temp.	Me-		Pr N N- 'Pr Co' Cl A	) 'Pr',,, 'Pr	
entry	catalyst	temp (°C)	Al/Co [mol ratio]	yield (%)	$M_{\rm w}~({\rm kg/mol})^b$	$M_{ m w}/M_{ m n}^{\ b}$	activity <sup>c</sup>
1	no catalyst	rt	1000	0			0
2	12	rt	0	0			0
3	12	60	1000	95	13.0	3.61	159
4	12	50	1000	92	12.0	3.07	154
5	12	40	1000	98	13.5	5.55	164
6	12	rt	1000	98	15.6	3.07	164
7	12	rt	800	96	13.5	3.59	159
8	12	rt	600	7	16.7	2.08	11.7
9	12	rt	400	trace			
10	Α	60	1000	trace			
11	Α	rt	1000	trace			

<sup>a</sup>Typical polymerization conditions: styrene 3.0 g; MAO (10 wt % in toluene); 8 mL of toluene. <sup>b</sup>Determined by GPC. <sup>c</sup>In units of (10<sup>5</sup> g of PS)/ [(mol of Co)  $\times$  h].

cobalt catalyst and cocatalyst MAO is essential for polymerization, the molar ratio of aluminum in MAO and cobalt catalyst 12 ([Al]/[Co]) was set at 1000. Initially, the reaction was run at 60 °C (entry 3). Surprisingly, the polymerization was too fast even at such a low catalyst loading and was completed in less than 1 h. The resulting polystyrene (PS) was isolated in 95% yield after precipitation in methanol. GPC analysis of the resulting polystyrene showed that the weight average molecular weight  $(M_w)$  was 13 000 g/mol and polydispersity  $(M_w/M_n)$  was 3.61. Catalyst activity was calculated to be 159 in units of 105 g of PS per 1 mol of catalyst per 1 h. This activity is remarkably high for a polystyrene polymerization catalyst.<sup>10a-d</sup> To optimize the reaction temperature, polymerizations were performed at lower temperatures (40 °C and rt; entries 5, 6). Surprisingly, the reactions did not deteriorate even at room temperature, and they provided polystyrene with almost the same molecular weight, polydispersity, and catalyst activity.

Since polymerization was fast enough even at room temperature, the reaction temperature was fixed at room temperature for the remaining experiments to optimize the amount of cocatalyst MAO (entries 7–9). Polymerization was not significantly affected until the amount of MAO was reduced to 800 [Al]/[Co] molar ratio. When the ratio was reduced to 400, the reaction was significantly affected, and only trace amounts of polystyrene were obtained (entry 8). These experiments showed that MAO cocatalyst is required with at least 800 molar equiv of cobalt catalyst 12 to achieve polymerization at room temperature.

As a comparison, Rosa's catalyst **A** was synthesized following the literature procedure.<sup>9</sup> Its catalytic activity was tested for styrene polymerization under the same reaction conditions (entries 10, 11). While catalyst **A** was reported to have some catalytic activity for ethylene polymerization, it showed very poor activity for styrene polymerization. Styrene polymerization did not proceed with Rosa's catalyst **A** even at 60 °C.

Styrene is one of only a few monomers that can be polymerized through all known polymerization mechanisms, including radical, anionic, cationic, and coordinated polymerizations. Each polymerization mechanism can lead to different stereoregularities. In some cases, the polystyrene obtained by transition metal catalyzed polymerization exhibits stereoselectivity showing enhanced tacticity control. For example, titanium catalysts reported by Natta and co-workers yielded isotactic polystyrene.<sup>12</sup> Other titanium catalysts have led to the synthesis of syndiotactic polystyrene.<sup>13a-e</sup> However, there are also many examples in which metal complexes exhibit poor or nonstereospecific polymerization. One example is the anilidoimino nickel/MAO catalytic system.<sup>14</sup> Although this catalyst was efficient for styrene polymerization and a coordination mechanism was proposed for the polymerization mechanism, the resulting polymer was atactic. The tacticities of the polystyrenes that were obtained with catalysts 6 and 12 were also investigated by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. Analysis of the spectra indicated that the polystyrenes obtained by these catalysts were atactic polymers. Free radical polymerization mechanisms were ruled out because a reaction that occurred in the presence of radical inhibitor TEMPO (N-oxy-2,2,6,6-tetramethylpiperidine) also provided polystyrene. In addition, an ethylene polymerization attempt with catalyst 12 under comparable conditions (800 equiv of MAO, 50 bar ethylene in toluene, 60 °C, 50 min) provided high-density polyethylene ( $T_{\rm m}$  = 138.3 °C) with a TON of 7720 h<sup>-1</sup> (see Supporting Information). We believe that this additional experiment supports that polystyrene was formed via a coordination polymerization mechanism rather than via a radical mechanism. A more detailed and systematic study of ethylene polymerization with catalyst 12 will be reported in due course.

#### CONCLUSIONS

Two new bis(amidine) ligand-based cobalt(II) complexes, **6** and **12**, were efficiently synthesized. The structure of **6** was verified by X-ray crystallography. The two complexes exhibited excellent activity for styrene polymerization up to  $164 \times 10^5$  g PS/(mol Co h) in the presence of cocatalyst MAO. Polymerization reactions proceeded very fast even at room temperature with high conversion (>99%), which is beneficial

for energy savings. Since the corresponding cobalt complex with a 1,2-dimine ligand did not exhibit styrene polymerization activity, the high catalytic activity of these catalysts was attributed to the enhanced electron donacity of the bis-(amidine) ligand. A future study will be undertaken to develop bis(amidine) ligand-based catalysts and screen catalyst activity by varying the core metals and structures of ligands.

#### EXPERIMENTAL SECTION

General Considerations. All reactions were carried out with dry, freshly distilled solvent under anhydrous conditions. Toluene was dried over sodium/potassium alloy for 48 h and freshly distilled under nitrogen before use. Styrene was purchased from Sigma-Aldrich, dried over calcium hydride, and then freshly distilled under vacuum before use. Methylaluminoxane (10 wt % Al) was generously provided by Prof. Bun Yeoul Lee's group at Ajou University. All reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. All experiments involving moisture- and/or air-sensitive compounds were performed in ovenand/or flame-dried glassware with rubber septa under positive pressure of argon using glovebox. Reactions were monitored by thin-layer chromatography (TLC) carried out on a 0.25 mm Merck silica gel plate (60F<sub>254</sub>) using UV light and p-anisaldehyde solution, phosphomolybdic acid solution (PMA), and/or ninhydrin solution, as a visualizing agent. Flash chromatography was performed using Merck 230-400 mesh silica gel. Melting points were determined using an electrothermal capillary melting point apparatus and are uncorrected. Infrared spectra were obtained on a Nicolet Avatar FT-IR spectrometer. NMR spectra were obtained either on Varian Inova-500 (500 MHz for <sup>1</sup>H, 125 MHz for <sup>13</sup>C) or Varian 400 (400 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C) NMR spectrometers. <sup>1</sup>H NMR spectra were referenced to tetramethylsilane ( $\delta$  0.00 ppm) as an internal standard and are reported as follows: s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet. <sup>13</sup>C NMR spectra were referenced to the residual CDCl<sub>3</sub> peak ( $\delta$  77.16 ppm). Elemental analyses were performed by the Organic Chemistry Research Center (OCRC) at

Sogang University using a Carlo Erba EA 1180 elemental analyzer. Synthesis of  $N^1$ , $N^2$ -Bis(2-isopropylphenyl)oxalamide (2). 2-Isopropylaniline (1, 5.24 mL, 37.0 mmol) and triethylamine (5.16 mL, 37.0 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (18.0 mL), and the solution was cooled to 0 °C. A solution of oxalyl chloride (1.42 mL, 16.8 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was added dropwise to the mixture with stirring, and ice bath cooling was applied over 1 h. The mixture was then allowed to stir at rt for 56 h. The mixture was transferred to a separatory funnel and then washed with water (~50.0 mL). The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic layers were evaporated to give a white solid. A solid was recrystallized from isopropyl alcohol to give 5.00 g of the desired oxalamide 2 (92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.52 (s, 2H), 8.05 (d, 2H, J = 4 Hz), 7.28–7.23 (m, 4H), 3.15 (m, 2H), 1.32 (d, 12H, J = 4 Hz).

Synthesis of  $(1Z,2Z)-N'^{1},N'^{2}$ -Bis(2-isopropylphenyl)oxalimidoyl Dichloride (3).  $N^{1},N^{2}$ -Bis(2-isopropylphenyl)oxalamide (2.00 g, 5.67 mmol) and phosphorus pentachloride (3.31 g, 12.5 mmol) were dissolved in toluene (8.42 mL). The mixture was heated at reflux over 30 min, then maintained at reflux for another 5 h to afford a clear yellow solution. The mixture was allowed to cool to rt and filtered, and the solvent evaporated to give a yellow solid. The resulting residue was purified by flash column chromatography on silica gel to give 1.50 g of the desired oxalimidoyl dichloride 3 (75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.39–7.37 (m, 2H), 7.28–7.25 (m, 2H), 7.00–6.97 (m, 2H), 3.10 (m, 2H), 1.25 (d, 12H, J = 4 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  143.53, 139.90, 137.89, 127.08, 126.76, 126.22, 126.09, 125.92, 125.79, 118.93, 118.67, 29.14, 28.98, 23.07, 22.90, 22.75, 22.59.

Synthesis of  $(1R,2R)-N^1,N^2$ -Dimethyl-1,2-diphenylethane-1,2-diamine (4). (4R,5R)-1,3-Dimethyl-2,4,5-triphenyl-1,3,2-diazaphospholidine 2-oxide  $(4.70 \text{ g}, 13.0 \text{ mmol})^8$  was dissolved in methanol (27.0 mL), and 0.8 M HCl/methanol (27.0 mL) was added to the solution. The resulting mixture was heated at reflux for 1 day. The pale yellow solution was cooled to rt, and the solvent evaporated to give a brown solid. Crystallization from isopropyl alcohol gave the diamine hydrochloride salt as a white crystalline solid. The salt was dissolved in saturated potassium carbonate solution and extracted into  $CH_2Cl_2$ . The organics were dried over potassium carbonate, filtered, and concentrated in vacuo to give the desired product 4 a white solid (1.60 g, 52%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.16–7.09 (m, 6H), 7.05–7.02 (m, 4H), 3.57 (s, 2H), 2.47 (br s, 2H), 2.26 (s, 6H).

Synthesis of (N,N'Z,N,N'Z)-N,N'-((5R,6R)-1,4-Dimethyl-5,6diphenylpiperazine-2,3-diylidene)bis(2-isopropylaniline) (5). Dimethyldiphenylethylenediamine (0.70 g, 2.91 mmol) and sodium bicarbonate (1.47 g, 17.5 mmol) were dissolved in THF (23.1 mL). The mixture was heated at 60 °C for 30 min, and N,N'-bis(2isopropylphenyl)oxalodiimidoyl dichloride (1.16 g, 3.20 mmol) in THF (23.1 mL) was added dropwise with stirring at 60 °C. The mixture was stirred at this temperature for a further 24 h. After cooling to rt it was filtered, and the solvent was evaporated to give a yellow solid. The resulting residue was purified by flash column chromatography on silica gel to give 0.50 g of the desired chiral bis(amidine) ligand 5 (34%). Mp: 95-98 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.43–6.64 (br m, 18H), 4.52 (br s, 2H), 3.40–2.60 (br, 5H), 2.20–1.70 (br, 3H), 1.22–0.68 (br, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 146.09, 142.05, 139.55, 137.70, 129.24, 128.28, 126.54, 124.95, 121.74, 118.99, 68.14, 37.51, 28.19, 26.43, 22.78. Anal. Calcd for C<sub>36</sub>H<sub>40</sub>N<sub>4</sub>: C, 81.78; H, 7.63; N, 10.6. Found: C, 81.65; H, 7.64; N, 10.57.

Synthesis of Chiral Bis(amidine) Cobalt(II) Complex (6). Isopropyl-bis(amidine) ligand (0.63 g, 1.20 mmol) and anhydrous cobalt chloride (0.15 g, 0.93 mmol) were dissolved in  $CH_2Cl_2$  (49.8 mL). The mixture was stirred at rt for 12 h, filtered, and concentrated in vacuo to give a sky blue solid. A solid was obtained either by recrystallization from  $CH_2Cl_2$  or precipitation in  $CH_2Cl_2/$ ether to give 0.43 g of the desired complex 6 (70%). Mp: 315–318 °C dec. Anal. Calcd for  $C_{36}H_{40}Cl_2CoN_4$ : C, 65.66; H, 6.12; N, 8.51. Found: C, 65.76; H, 6.07; N, 8.32.

**Synthesis of 2,3-Dihydroxyquinoxaline (8).** A solution of oxalic acid (13.6 g, 108 mmol) in 4 N aqueous HCl (25.0 mL) was added to a solution of 1,2-diaminobenzene (10.6 g, 97.7 mmol) in 4 N HCl (75.0 mL), and the resulting solution was heated at reflux for 2 h. The reaction mixture was cooled to ambient temperature, and the resulting precipitate was isolated by filtration, washed with water, and dried, giving 15.5 g (98%) of 8 as an off-white powder. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  11.92 (s, 2H), 7.15–7.05 (m, 4H). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  155.17, 125.55, 122.93, 115.10

Synthesis of 2,3-Dichloroquinoxaline (9). *N*,*N*-Dimethylformamide (0.01 mL, 0.19 mmol) was added dropwise to slurry of 2,3dihydroxyquinoxaline (3.00 g, 18.5 mmol) and thionyl chloride (3.50 mL, 48.1 mmol) in 1,2-dichloroethane (31.0 mL). The resulting reaction mixture was heated to reflux for 2 h, then concentrated to dryness. The residue was dissolved in 1,2-dichloroethane (35.0 mL) and concentrated to dryness. The resulting solid was recrystallized from CH<sub>3</sub>CN/H<sub>2</sub>O, giving 3.50 g (96%) of **9** as an off-white needles. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.12–8.08 (m, 2H), 7.99–7.94 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.57, 139.97, 131.71, 127.84.

Synthesis of  $N^2$ , $N^3$ -Bis(2-isopropylphenyl)quinoxaline-2,3diamine (10). Under a nitrogen atmosphere, 2,3-dichloroquinoxaline (1.00 g, 5.00 mmol) and 2-isopropylaniline (3.50 mL, 25.0 mmol) in a sealed tube were heated at 150 °C for 2 h. The resulting residue was purified by flash column chromatography on silica gel, and then the desired product was obtained in 1.63 g (82%) yield as a yellow powder. Mp: 113–115 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.10 (br s, 1H), 8.60 (br s, 1H), 7.65 (br s, 1H), 7.33–6.76 (br m, 10H), 6.29 (br s, 1H), 3.07 (br s, 2H), 1.10 (br d, 12H, J = 40 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  146.46, 144.33, 141.50, 137.67, 137.21, 136.06, 132.54, 127.10, 126.88, 126.33, 126.15, 125.30, 124.48, 123.57, 122.95, 121.21, 120.34, 113.35, 28.42, 28.13, 23.02, 22.74.

Synthesis of (N,N'Z,N,N'Z)-N,N'-(1,4-Dimethylquinoxaline-2,3(1H,4H)-diylidene)bis(2-isopropylaniline) (11). To a solution of  $N^2$ , $N^3$ -bis(2-isopropylphenyl)quinoxaline-2,3-diamine (2.40 g, 6.00 mmol) in DMSO (50.0 mL) was added NaH (0.70 g, 30.0 mmol), and

the reaction mixture was stirred at rt for 10 min. Methyl iodide (1.90 mL, 30.0 mmol) was added, and the reaction mixture was stirred at rt for 1 h. The reaction was quenched by careful addition of MeOH and diluted with an ice and water mixture. The product was then extracted with methylene chloride, and the combined organic layers were washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuo. The crude residue was purified by flash column chromatography on silica gel to give the desired product in 1.70 g (67%) yield as a dark yellow powder. Mp: 139–141 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.06–6.89 (br m, 10H), 6.42 (br s, 2H), 3.31 (br, 8H), 0.97 (br s, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  145.84, 140.03, 136.73, 130.73, 129.51, 125.54, 125.24, 122.89, 121.72, 118.93, 115.15, 112.72, 105.92, 32.96, 27.75, 23.05.

Synthesis of Bis(amidine) Cobalt(II) Complex (12). (N,N'Z,N,N'Z)-N,N'-(1,4-Dimethylquinoxaline-2,3-(1H,4H)-diylidene)bis(2-isopropylaniline) (0.20 g, 0.47 mmol) and anhydrous cobalt chloride (0.06 g, 0.46 mmol) were dissolved in EtOH (10.0 mL). The reaction mixture was heated at reflux for 12 h, filtered, and concentrated in vacuo to give a green solid. The resulting solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexanes, giving 0.20 g (88%) of dark green needles. Mp: 168–175 °C. Anal. Calcd for C<sub>28</sub>H<sub>32</sub>Cl<sub>2</sub>CoN<sub>4</sub>: C, 60.66; H, 5.82; N, 10.11. Found: C, 60.52; H, 5.92; N, 9.97.

**Polymerization of Styrene.** The polymerizations of styrene were conducted in 25 mL Schlenk tubes that were flamed under vacuum and backfilled with argon. The desired amounts of solvent (toluene), styrene, and catalyst suspension in the solvent (16  $\mu$ M) were injected in this order via a syringe. The polymerization was then initiated by addition of MAO in toluene via a syringe. After the desired reaction time, the reaction mixture was dripped into the mixture of concentrated hydrochloric acid and methanol [5:95 (v/v)] to precipitate polystyrene. The white precipitates were isolated by filtration, washed with methanol, and dried under vacuum at 60 °C to give polystyrene.

# ASSOCIATED CONTENT

#### **Supporting Information**

X-ray crystallographic data of **6** including CIF files, <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5**, **10**, and **11**, <sup>1</sup>H NMR monitoring data of styrene polymerization with catalyst **12**, <sup>13</sup>C NMR of the polystyrene obtained by catalyst **12**, synthetic procedure of chiral bis(amidine) Ni(II) complex, and ethylene polymerization procedure with catalyst **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest. <sup>§</sup>Deceased on Nov 9, 2012.

# ACKNOWLEDGMENTS

This work was supported by the Sogang University Research Grant of 2010 (201010032.01) and by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MOE) (NRF-2012R1A1A2009532).

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