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C_1-Symmetric Pentacoordinate Anilidopyridylpyrrolide Zirconium(IV) Complexes as Highly Isospecific Olefin Polymerization Catalysts

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ABSTRACT: Two new anilinepyridinepyrrole ligand precursors bearing bulky substituents on the carbon bridging the pyridine and the aniline moieties were synthesized and used to prepare the corresponding zirconium complexes with general formula [$^-$NNN$^-$]Zr(NMe$_2$)$_2$. NMR spectra analysis of the obtained complexes indicated a C_1-symmetry in solution. Both complexes were tested as precatalysts for ethylene and α-olefins polymerization upon activation with Al^{i}Bu$_2$H as alkylating agent and MAO as ionizing activator. Linear polyethylene and highly isotactic polypropylene and poly(1-hexene) were obtained with good productivities. In particular, the features of the obtained polypropylene samples, in terms of isotacticity ([*mmmm*] up to 95%), molecular weight (M_w up to 950 kg/mol) and melting point (T_m up to 150 °C), were remarkable. The activity and the isospecificity of this class of catalysts were found to depend strongly on the steric bulk of the substituents on the carbon bridging the pyridine and aniline moieties.

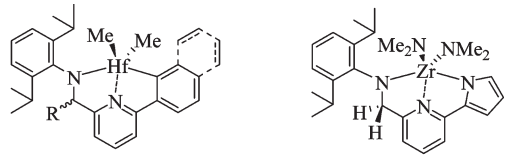
Introduction

The design of nonmetallocene catalysts for olefin polymerization with high activities and stereoselectivities remains a topic of wide interest in both academic and industrial research.[1,2] In particular, a large variety of ligands with nitrogen and/or oxygen donors has been explored, leading to several highly isospecific catalysts, e.g., diaminebis(phenolate) group 4 metal[3] and bis(phenolate)diether Zr or Hf catalysts,[4] although in only a few cases their performance is competitive with the metallocene systems.[5]

A promising class of catalysts based on C_1-symmetric pyridylamido Hf(IV) complexes (Scheme 1) was recently developed using high throughput screening technologies.[6] These catalysts are able to produce high molecular weight, highly isotactic propylene homo- and copolymers at high temperatures, as well as olefin block copolymers with good elastomeric properties.[7] A fundamental aspect for the achievement of these performance was the serendipitous modification of the ligand structure via metalation of an aromatic substituent in the pyridine *ortho* position, changing a [NN$^-$] monoanionic bidentate ligand in a [$^-$NNC$^-$] dianionic tridentate one (Scheme 1). Moreover, an increasing amount of experimental and theoretical evidence suggested that further *in situ* modification of the precatalyst via a first monomer 1,2-insertion into Hf−C$_{aryl}$ bond is involved in the generation of highly active and stereospecific catalytic species.[8] It was also mentioned that bulkier substituents on the carbon bridging the amide and the pyridine fragment gave catalysts with better performance.[6i]

Recently, we reported the synthesis of Zr(IV) complex **1** (Scheme 1), bearing an anilidomethylpyridylpyrrolide [$^-$NNN$^-$] tridentate ligand, which, after activation with Al^{i}Bu$_2$H/MAO, produced isotactic polypropylene ([*mmmm*] = 73%) as well as isotactic poly(1-hexene) with good activities.[9] Complex **1** showed a slightly distorted square-pyramidal geometry in the solid state and "time averaged" C_s-symmetric structure in solution: however, despite the precatalyst structure, isotactic polyolefins with a microstructure consistent with an "*enantiomorphic sites*" mechanism of steric control were produced. A similar finding had been previously reported by Coates et al.[10] for a C_s-symmetric pyridylamido [$^-$NNC$^-$] Hf(IV) complex, and in that case *in situ* ligand modification due to insertion of one propene molecule into the Hf-aryl bond was suggested to justify the unexpected isoselectivity. Since in the case of complex **1** insertion of one monomer unit into a Zr−pyrrolyl bond is unlikely, the origin of its isospecificity remains elusive, being attributable, e.g., to other ligand modifications or to a change of hapticity in the pyrrole moiety or even to a preferred square pyramidal geometry of the cationic active species resulting in two inequivalent coordination sites for the olefin and the growing chain.

Scheme 1



(pyridylamido)Hf(IV) complexes complex **1**

Seeking to expand the scope of this class of ligands for the design of stereospecific catalysts and to achieve some insight in the factors affecting their performance, we have now synthesized two new anilinepyridinepyrrole ligands bearing bulky substituents on the carbon bridging the pyridine and the aniline moieties, and two C_1-symmetric Zr(IV) complexes derived thereof, and tested them as olefin polymerization catalysts.

Results and Discussion

The anilinepyridinepyrrole ligands (H_2L^1, H_2L^2) were synthesized by alkylation of anilinemethylenepyridinepyrrole **A**[9] (Scheme 2) with an excess of alkylating agents (PhLi or 2-iPrC$_6$H$_4$Li) in good yields, and fully characterized by NMR spectroscopy. Complexes **2** and **3** were prepared in benzene by reaction of the corresponding ligand with equimolar amount of tetrakis(dimethylamido)-zirconium(IV) and isolated as light-yellow solids (yields: **2**: 93%; **3**: 76%). (Scheme 2) The complexes were also fully characterized by NMR spectroscopy. In the ^{1}H NMR spectrum of each

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Scheme 2. Synthesis of the Zr Complexes

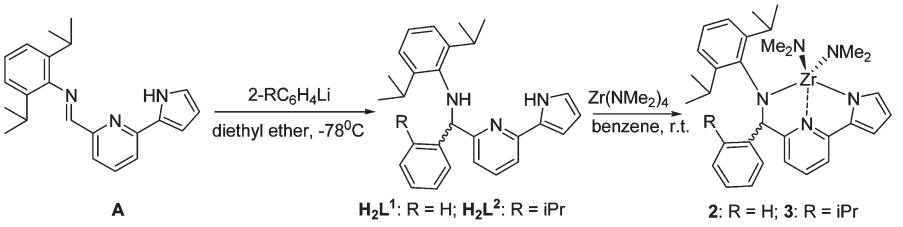

Table 1. Ethylene Polymerization Results[a]

run	precat.	activity[b]	T_m (°C)	M_w (kg/mol)	PDI
1[9]	**1**	1841	136.5	185	2.1
2	**2**	1035	135.1	49	3.8
3	**3**	905	136.0	n.d.[c]	n.d.[c]

[a] General conditions: precatalyst, 2.5 μmol; toluene, 100 mL; cocatalyst, $Al^iBu_2H/Zr = 30$, $Al_{(MAO)}/Zr = 1000$; aging time, 10 min; ethylene pressure, 1 atm; polymerization time, 7 min; polymerization temperature, 25 °C; dried MAO obtained by distilling off the solvent from the commercial solution. [b] Activity: kg_{PE}/mol Zr h atm. [c] n.d. = not determined.[12]

complex (Figure S5 and S7 in the Supporting Information), different signals were present for each proton, indicating a C_1-symmetry in solution. In particular, two singlets for the Zr-NMe_2, and four doublets and two septets for the isopropyl groups of the aniline moiety were detected. ^{13}C NMR spectra analysis led us to the same conclusion. (Figure S6 and S8 in the Supporting Information).

Ethylene and α-Olefin Polymerization. All complexes were used as precatalysts in combination with Al^iBu_2H as alkylating agent (in view of the well-known difficult alkylation of dimethylamido group 4 complexes by MAO alone)[11] and MAO as ionizing activator for ethylene and α-olefins polymerization. Ethylene polymerization data are listed in Table 1. After activation with Al^iBu_2H/MAO, **2** and **3** promote polymerization of ethylene to highly linear polyethylene with good productivities. In comparison with the unsubstituted complex **1**, introduction of bulky substituents on the bridging methylene atom resulted in slight decreases of productivities and polymer melting points (T_m), and in a significant decrease of molecular weights (M_w = 49 kg/mol for **2**). A rather broad molecular weight distribution (PDI: 3.8 for **2**) (Table 1, run 2) was also observed.[12] Broad molecular weight distributions were also reported for ethylene polymerization by pyridylamido Hf catalysts.[8a,13]

Polymerization of propene was also investigated: the main polymerization data and results are listed in Table 2. After activation with Al^iBu_2H/MAO under 6 atm monomer pressure at 25 °C, the precatalyst **2** yielded highly isotactic polypropylene ([*mmmm*] = 87.2%) having a melting point T_m = 131 °C with good activity (activity: 38.8 kg_{PP}/mol_{Zr} h atm) (run 2, Table 2). GPC analysis of the obtained polypropylene sample exhibited a broad molecular weight distribution (PDI = 5.6). Compared with precatalyst **1** under the same conditions, precatalyst **2**, bearing a phenyl substituent on the bridging methylene, displayed a 10-fold increase of productivity, a 4-fold increase of molecular weight, and higher stereoselectivity ([*mmmm*] = 87.2 vs 73%). A further increase of the steric bulk of the substituent of the bridging methylene led to a better performing catalyst: under the same conditions, precatalyst **3** exhibited higher productivity (activity: 97.6 kg_{PP}/mol_{Zr} h atm) (run 3, Table 2), and higher stereoselectivity ([*mmmm*] = 94.5%), affording a polypropylene with a melting point T_m = 150 °C. GPC analysis of the obtained polypropylene sample displayed ultrahigh molecular weight (950 kg/mol) with a rather broad molecular weight distribution

Table 2. Propylene Polymerization Results[a]

run	precat	activity[b]	[*mmmm*] (%)	regioinverted units	T_m (°C)	M_w (kg/mol)	PDI
1[9]	**1**	4	73	3.0		39	1.4
2	**2**	39	87.2	2.1	131	166	5.6
3	**3**	98	94.6	1.4	150	950	3.5
4[c]	**3**	14	93.1	2.4	140	16	2.2
5[d]	**3**	27	94.1	1.9	150	404	12.4
6[e]	**3**	49	95.0	1.6	151	1012	1.9
7[f]	**3**	99	95.3	1.5	151	195	4.6

[a] General condition: precatalyst, 10 μmol; toluene, 100 mL; cocatalyst, $Al^iBu_2H/Zr = 30$, $Al_{(MAO)}/Zr = 1000$; dried MAO obtained by distilling off the solvent from the commercial solution; aging time, 10 min; polymerization temperature, 25 °C; polymerization time, 60 min; propylene pressure, 6 atm. [b] Activity: kg_{PP}/mol Zr h atm. [c] Polymerization temperature: 75 °C. [d] Propylene pressure: 2 atm. [e] $Al^iBu_2H/Zr = 10$. [f] Polymerization time: 10 min.

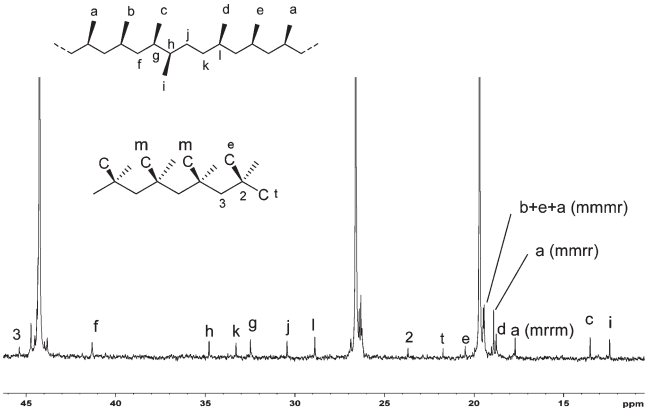

Figure 1. ^{13}C NMR spectrum (1,1,2,2-tetrachloroethane-d_2,100 °C) of *i*-PP produced in run 4 in Table 2. δ in parts per million from hexamethyldisiloxane.

(PDI = 3.5). Thus, the performance of **3**/Al^iBu_2H/MAO catalyst for propene polymerization, in terms of isotacticity and T_m, competes with that of the best nonmetallocene catalysts reported in the literature, although the hafnium pyridyl-amido-based catalysts are more active and afford higher MW's at high temperature.[14]

^{13}C NMR analysis of the stereosequence distribution of the obtained polypropylene samples produced by both **2** and **3** showed a 2:2:1 ratio of the [*mmmr*]/[*mmrr*]/[*mrrm*] pentads in the methyl region, in agreement with an "*enantiomorphic sites*" mechanism of the stereospecific propagation.[2,5,15] Minor resonances (12.4, 13.5, 28.8, 30.4, 32.3, 33.2, 34.6, and 41.2 ppm) (Figure 1) are attributed to isolated regiodefects, deriving from head-to-head or tail-to-tail misinsertions.[6i,16] The exclusive presence of regioinverted units with vicinal methyls in *threo* configuration in the Fischer projection[17] indicates that primary (1,2) and secondary (2,1) monomer insertions occur with the same enantioface selectivity, as previously observed for **1** and other nonmetallocene catalysts,[6i,16b]

Table 3. 1-Hexene Polymerization Results[a]

run	precat	T (°C)	yield (mg)	[*mmmm*] (%)	M_w (kg/mol)	PDI
1	**2**	25	230	99	13	2.1
2	**2**	50	138	93	5	2.1
3	**3**	25	457	>99	37	2.0

[a] General conditions: precatalyst = 5 μmol; toluene, 5 mL, 1-hexene, 5 mL; cocatalyst, $Al^iBu_2H/Zr = 30$, MAO/Zr = 1000; aging time, 10 min; polymerization time, 60 min.

while the opposite enantioface selectivity occurs for primary and secondary insertions in C_2-symmetric metallocene catalysts.[2,5]

Polymerization at higher temperature (75 °C) results in the production of a polypropylene sample having a significantly lower molecular weight (16 kg/mol) and a narrower molecular weight distribution (PDI = 2.2), while the stereoregularity is only slightly affected, ([*mmmm*] = 93.1%, T_m = 140 °C, see Table 2, run 4). An increase of regioinversions is also observed (from 1.4 to 2.4%, Table 2, cf runs 3 and 4). In this low M_w sample, additional low intensity resonances are detected at 45.4, 23.7, 21.8, 20.5 ppm: they are attributable, according to the literature,[18] to isobutyl end groups, reasonably deriving from primary (1,2) propene insertion into Zr−Me or Zr−^{i}Bu bonds in the initiation step or from hydrolysis of Zr- and/or Al-bound primary growing chains in the termination step.

We also investigated the influence of other polymerization conditions, i.e., monomer pressure, amount of Al^iBu_2H, and polymerization time, on the performance of **3** (Table 2, run 5, 6, and 7, respectively). None of these parameters affects significantly the polymer microstructure,[19] while a strong influence on the polymer M_w's is observed. In fact, lowering the amount of Al^iBu_2H from 30 to 10 equiv resulted in a narrower molecular weight distribution (PDI = 1.9) and similar isotacticity (*mmmm* = 95.0%, T_m = 151 °C), suggesting that broad MWD's could be due to chain transfer to aluminum having different rates during the polymerization.[20] In agreement with this hypothesis, a shorter polymerization time (10 vs 60 min) resulted in the production of a polymer sample exhibiting a relatively broader molecular weight distribution (PDI = 4.6). Finally, reducing the monomer pressure from 6 to 2 atm resulted in the production of a polypropylene sample having a very broad molecular weight distribution (PDI = 12.4).

In order to further investigate the origin of the broadening of MWD's, a polypropylene sample (run 3, Table 2) was fractionated by sequential exhaustive Kumagawa extraction with boiling *n*-hexane and *n*-heptane. Analysis of the different fractions by GPC, NMR and DSC (see Supporting Information) showed that, although fractions with different molecular weights were recovered, the isotacticity was very high and very similar in all cases, excepting for a small fraction (<9%) soluble in *n*-hexane, having low isotacticity and low molecular weight. In conclusion, while the hypothesis that broad MWD's are mainly due to chain transfer to Al seems confirmed, these data also suggest the possible formation of some minor active species having different polymerization performance.

We also studied the behavior of precatalysts **2** and **3** in 1-hexene polymerization. After activation with Al^iBu_2H/MAO, the precatalysts **2** − **3** yielded moderate activities and polymerized 1-hexene to regioregular and isotactic poly(1-hexene) with narrow molecular weight distribution (PDI: 2.1 for **2**; 2.0 for **3**, respectively). The poly(1-hexene) sample produced by **2**/Al^iBu_2H/MAO at 25 °C polymerization temperature exhibited a good isotacticity ([*mmmm*] = 99%) and a rather low molecular weight (13 kg/mol) (Table 3, run 1). Increasing the polymerization temperature to 50 °C resulted in decrease of both isotacticity and molecular weight. However, the poly(1-hexene) sample produced by **3**/Al^iBu_2H/MAO showed almost perfect isotacticity ([*mmmm*] > 99%): resonances attributable to stereodefects and to end groups were not detected (Figure 2).

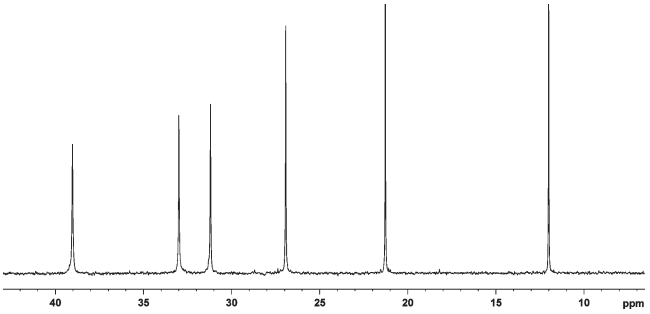

Figure 2. ^{13}C NMR spectrum (1,1,2,2-tetrachloroethane-d_2,100 °C) of Poly(1-hexene) produced in run 3 in Table 3; δ in parts per million from hexamethyldisiloxane.

Conclusions

Two new tridentate anilinepyridinepyrrole ligands H_2L, bearing bulky substituents on the carbon bridging the pyridine and the aniline moieties, and their C_1-symmetric LZr(IV) bis(dimethylamido) complexes have been synthesized and tested as precatalysts for olefin polymerization, after activation with Al^iBu_2H/MAO. Linear polyethylene and highly isotactic polypropylene and poly(1-hexene) were obtained with good productivities. Interestingly, in comparison with the previously reported unsubstituted anilidomethylpyridinepyrrolide Zr(IV) complex,[9] introduction of bulky substituents on the bridging methylene in the ligand framework lead to propylene polymerization catalysts performing much better in terms of activity, polymer isotacticity and molecular weight. E.g., the complex bearing a 2-isopropylphenyl substituent afforded a polymer having M_w close to 1 million Da, [*mmmm*] > 95% and melting temperature as high as 151 °C, which are remarkable values for polypropylenes produced by homogeneous catalysts.

^{13}C NMR analysis of the obtained polypropylenes revealed a microstructure in agreement with the "*enantiomorphic sites*" mechanism of the stereospecific propagation, as well as the occurrence of a few regioinverted units having vicinal methyls in *threo* configuration,[17] thus indicating that primary and secondary monomer insertions occur with the same enantioface selectivity, as previously observed for other nonmetallocene catalysts.[6i] Finally, the detection of isobutyls as the only end groups in low MW samples suggested that 1,2 insertion is the main regiochemistry of propagation.

The MWD's of the polypropylene samples range between that expected for a single site catalyst and broader ones, depending on the polymerization conditions and, in particular, on the amount of Al^iBu_2H. The latter and other lines of evidence suggest that broadening of MWD's could be mainly due to chain transfer to aluminum having different rates during the polymerization. Work is in progress to synthesize complexes of this class bearing mobile ligands different from NMe_2, amenable to be activated without using aluminum alkyls, in order to reduce chain transfer and possibly achieve living polymerization.

Experimental Section

General Procedures. All manipulations of air- and or water-sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk or glovebox techniques. All solvents, purchased from Carlo Erba, were refluxed over sodium/benzophenone or calcium hydride (CaH_2) and then distilled under nitrogen before use. 1-Bromo-2-isopropylbenzene was purchased from Alfa Aesar without purification before use. All other chemicals were purchased from Sigma-Aldrich and used

as received. MAO (10 wt % solution in toluene) was dried by distilling off the volatile materials under reduced pressure and excess of trimethylaluminium ($AlMe_3$) was removed by washing the resulting solid with dry hexane. The volatiles were removed under reduced pressure to obtain a white powder. Ethylene and propene were purchased from SON and used without further purification. 1-Hexene was distilled over CaH_2 prior to use.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance spectrometer at 400 and 100.6 MHz. ^{13}C NMR spectra of polymers were recorded on a Bruker AM-250 spectrometer at 62.5 MHz in 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$) at 100 °C and referenced vs hexamethyldisiloxane (HMDS).

Molecular weights (M_n and M_w) and polydispersities (PDI) of the polymers were determined by high-temperature GPC using a Waters GPCV 2000 equipped with refractive index and viscometer detectors. The measurements were recorded at 135 °C using 1,2-dichlorobenzene as a solvent and Styragel columns (range 10^7 to 10^3). Every value was the average of two independent measurements.

Polymers melting points (T_m) were measured by differential scanning calorimetry using a TA Instruments DSC 2920 in nitrogen flow with a heating and cooling rate of 10 °C/min. Melting temperatures were reported for the second heating cycle.

Synthesis of Ligands. (*E*)-*N*-(6-(1*H*-Pyrrol-2-yl)pyridin-2-yl)-methylene)-2,6-diisopropylbenzenamine was synthesized according to the literature.[9]

N-((6-(*1H-Pyrrol-2-yl*)*pyridine-2-yl*)(*phenyl*)*methyl*)-*2,6-diisopropylbenzenamine* (*H_2L^1*). A solution of PhLi (0.58 mL, 1.08 mmol, 1.9 M in nBu_2O) was added dropwise into a solution of (*E*)-*N*-(6-(1*H*-pyrrol-2-yl)pyridin-2-yl)methylene)-2,6-diisopropylbenzenamine (180 mg, 0.54 mmol) in diethyl ether (2 mL) cooled to −78 °C. Then, the solution was allowed to warm to room temperature and stirred for 20 h. The reaction was followed by TLC and then quenched by the addition of NH_4Cl (aq) at 0 °C. The organic phase was separated and reserved. The aqueous phase was washed by diethyl ether (3 × 30 mL). The combined organic phases were washed using water (2 × 50 mL), and brine (1 × 50 mL), and then dried over Na_2SO_4. The solvent was distilled off by rotary evaporation. The crude product was purified by flash column chromatography on silica gel using hexane/diethyl ether (20/1, 9/1) as eluent. The colorless oil was concentrated in vacuum, obtaining a white powder (158 mg, yield: 73%). ^1H NMR (CD_2Cl_2): δ 0.97 (6H, d, J = 6.8 Hz, CH(CH_3)$_2$), 1.07 (6H, d, J = 6.8 Hz, CH(CH_3)$_2$), 3.12 (2H, sept, CH(CH$_3$)$_2$), 4.78 (1H, br, s, NHCHPh), 5.11 (1H, s, NCHPh), 6.28 (1H, m, NC$_4H_3$), 6.72 (1H, m, NC$_4H_3$), 6.90−6.92 (1H, m, NC$_4H_3$), 6.94−6.99 (3H, m, *H*−Ar), 7.01 (1H, d, J = 3.6 Hz, *H*−Py), 7.19−7.31(3H, m, *H*−Ar), 7.39−7.42 (2H, m, *H*−Ar), 7.43 (1H, d, J = 0.96 Hz, *H*−Py), 7.55 (1H, t, *H*−Py), 9.50 (1H, br, s, HNC$_4H_3$). ^{13}C NMR (CD_2Cl_2): δ 24.28 (d, J = 20.22 Hz, CH(CH_3)$_2$), 28.18 (CH(CH$_3$)$_2$), 69.76 (NHCHPh), 107.85, 110.75, 116.93, 119.72, 120.29, 123.66, 123.99, 127.45, 127.82, 128.69, 131.88, 137.55, 142.60, 142.95, 143.67, 148.51, 150.66, 161.59.

N-((6-(*1H-Pyrrol-2-yl*)*pyridine-2-yl*)(*2-isopropylphenyl*)*methyl*)-*2,6-diisopropylbenzenamine* (*H_2L^2*). *n*-Butyl lithium (0.35 mL, 0.88 mmol, 2.5 M in hexane) was added to a solution of 1-bromo-2-isopropylbenzene (162 mg, 0.81 mmol) in dry diethyl ether (5 mL) cooled to 0 °C. The colorless solution was warmed to room temperature and stirred for 3 h. Then, the solution was added dropwise to a dry diethyl ether (2 mL) solution of (*E*)-*N*-(6-(1*H*-pyrrol-2-yl)pyridin-2-yl)methylene)-2,6-diisopropylbenzenamine (100 mg, 0.30 mmol) at −78 °C. The yellow solution was warmed to room temperature and stirred for 30 min. The color turned to red. The reaction was followed by TLC and then quenched with NH_4Cl (aq) at 0 °C. The organic phase was separated and reserved. The aqueous phase was washed with diethyl ether (3 × 30 mL). The combined organic phases were extracted with water (2 × 30 mL) and brine (1 × 30 mL). The organic phase was dried over Na_2SO_4. The solvent was distilled off by rotary evaporation. The crude product was purified by flash column chromatography on silica gel using hexane/diethyl ether (20/1) as eluent. The colorless oil was concentrated under vacuum (120 mg, yield: 88%). ^1H NMR (CD_2Cl_2): δ 0.95−0.98 (12H, m, CH(CH_3)$_2$), 1.01 (6H, d, J = 9.14 Hz, CH(CH_3)$_2$), 2.89 (2H, sept, CH(CH$_3$)$_2$), 3.04 (1H, sept, CH(CH$_3$)$_2$), 4.24 (1H, br, s, NHCHPh), 5.42 (1H, s, NCHPh), 6.23 (1H, m, NC$_4H_3$), 6.67 (1H, m, NC$_4H_3$), 6.84 (1H, m, NC$_4H_3$), 6.94 (1H, m, *H*−Py), 7.00−7.03 (3H, m, *H*−Ar), 7.24 (3H, m, *H*−Ar), 7.37 (1H, m, *H*−Py), 7.54 (1H, t, *H*−Py), 7.66 (1H, m, *H*−Ar), 9.26 (1H, br, s, HNC$_4H_3$). ^{13}C NMR (CD_2Cl_2): δ 23.96 (CH(CH_3)$_2$), 24.23 (CH(CH_3)$_2$), 24.37 (CH(CH_3)$_2$), 28.27 (CH(CH_3)$_2$), 29.09 (CH(CH$_3$)$_2$), 66.53 (NHCHPh), 107.58, 110.70, 116.54, 118.88, 120.16, 123.94, 124.03, 126.00, 126.40, 127.83, 127.89, 132.02, 137.62, 140.45, 142.98, 143.36, 146.84, 150.36, 162.57.

Synthesis of Complexes. *Zr Complex* (*2*). A solution of $Zr(NMe_2)_4$ (103 mg, 0.38 mmol) in benzene (5 mL) was added dropwise into a stirred solution of H_2L^1 (158 mg, 0.38 mmol) in benzene (5 mL). The solution was stirred for 30 min at room temperature. All volatiles were removed under vacuum. The product was crystallized from hexane (1 mL) at −20 °C, and washed with hexane, obtaining a light yellow solid (208 mg, yield: 93%). ^1H NMR (400 MHz; $CDCl_3$): δ 0.15 (3H, d, J = 6.84 Hz, CH(CH_3)$_2$), 1.04 (3H, d, J = 6.84 Hz, CH(CH_3)$_2$), 1.07 (3H, d, J = 6.84 Hz, CH(CH_3)$_2$), 1.33 (3H, d, J = 6.84 Hz, CH(CH_3)$_2$), 2.60 (6H, s, ZrN(CH_3)$_2$), 2.84 (1H, sept, CH(CH$_3$)$_2$), 2.95 (6H, s, ZrN(CH_3)$_2$), 3.24 (1H, sept, CH(CH$_3$)$_2$), 5.58 (1H, s, NCHPh), 6.32 (1H, m, NC$_4H_3$), 6.58 (1H, d, J = 7.6 Hz, *H*−Py), 6.80 (1H, m, NC$_4H_3$), 6.92−6.94 (3H, m, Ar−*H*), 7.05 (1H, t, Ar−*H*), 7.11 (1H, m, Ar−*H*), 7.16 (1H, m, NC$_4H_3$), 7.18−7.21(3H, m, Ar−*H*), 7.37 (1H, d, J = 7.92 Hz, *H*−Py), 7.63 (1H, t, *H*−Py). ^{13}C NMR (300 MHz; $CDCl_3$): δ 24.15 (CH(CH_3)$_2$), 24.64 (CH(CH_3)$_2$), 25.03 (CH(CH_3)$_2$), 26.91 (CH(CH_3)$_2$), 27.64 (CH(CH$_3$)$_2$), 28.47 (CH(CH$_3$)$_2$), 40.96 (N(CH_3)$_2$), 42.42 (N(CH_3)$_2$), 80.81 (NCHPh), 109.18 (NC_4H_3), 111.73 (NC_4H_3), 114.46 (*C*−Py), 116.37 (*C*−Py), 123.61, 124.12, 124.28, 127.54, 128.64, 129.07, 133.15, 140.30, 140.40, 143.97, 145.96, 146.57, 146.98, 154.87, 167.27.

Zr Complex (*3*). A solution of $Zr(NMe_2)_4$ (42 mg, 0.157 mmol) in benzene (3 mL) was added dropwise into a stirred solution of H_2L^2 (71 mg, 0.157 mmol) in benzene (5 mL). The solution was stirred for 30 min at ambient temperature. All volatiles were removed under vacuum to yield a yellow solid. The product was crystallized from hexane (1 mL) at −20 °C and then washed with hexane. The light yellow solid was obtained in 76% yield (75 mg, 0.119 mmol). ^1H NMR (400 MHz; $CDCl_3$): δ 0.13 (3H, d, J = 6.84 Hz, CH(CH_3)$_2$), 0.58 (3H, d, J = 6.84 Hz CH(CH_3)$_2$), 1.02−1.07 (9H, m, CH(CH_3)$_2$), 1.29 (3H, J = 6.72 Hz, CH(CH_3)$_2$), 2.50 ((1H, m, CH(CH$_3$)$_2$), 2.62 (6H, s, N(CH_3)$_2$), 2.88 (1H, m, CH(CH$_3$)$_2$), 3.00 (6H, s, N(CH_3)$_2$), 3.30 (1H, m, CH(CH$_3$)$_2$), 5.96 (1H, s, NCHPh), 6.32 (1H, m, NC$_4H_3$), 6.46 (1H, d, J=7.64 Hz, *H*−Py), 6.79 (1H, m, NC$_4H_3$), 6.94 (1H, m, Ar−*H*), 7.01 (1H, t, Ar−*H*), 7.07−7.19 (6H, m, Ar−*H*), 7.33 (1H, d, J = 7.92 Hz, *H*−Py), 7.56 (1H, t, *H*−Py). ^{13}C NMR (400 MHz; $CDCl_3$): δ 22.08 (CH(CH_3)$_2$), 23.75 (CH(CH_3)$_2$), 24.98 (CH(CH_3)$_2$), 25.55 (CH(CH_3)$_2$), 25.77 (CH(CH_3)$_2$), 26.04 (CH(CH_3)$_2$), 27.75 (CH(CH$_3$)$_2$), 28.32 (CH(CH$_3$)$_2$), 28.60 (CH(CH_3)$_2$), 41.16 (ZrN(CH_3)$_2$), 42.77 (ZrN(CH_3)$_2$), 74.95 (NCHPh), 109.11 (NC_4H_3), 111.75 (NC_4H_3), 114.15 (*C*-Py), 116.09 (*C*-Py), 123.75, 124.28, 124.51, 125.25, 126.25, 127.44, 130.17, 133.13, 140.43, 141.43, 145.80, 146.65, 147.11, 147.26, 154.81, 168.69.

Polymerizations Procedure. *General Procedure for Ethylene and Propylene Polymerization.* The polymerizations were carried out in a magnetically stirred flask (250 mL) or in a Büchi glass autoclave (500 mL). Under a nitrogen atmosphere, the required equivalents of Al^{i}Bu$_2$H were added to a solution of the complexes in toluene (2 mL) and then stirred for 10 min at room temperature. The reactor vessels were charged sequentially with toluene, dried MAO and a solution of the precatalyst in toluene. The stirred mixture was thermostated at the required temperature, and then the monomer gas feed was started. After the prescribed time, the

polymerization mixture was poured into acidified ethanol. The polymers were filtered, washed with ethanol, and dried in a vacuum oven at 40 °C overnight.

General Procedure for 1-Hexene Polymerization. Polymerizations were carried out in a magnetically stirred flask (50 mL). Under a nitrogen atmosphere, Al^iBu_2H (150 μmol) was added to a solution of complex (5 μmol) in toluene (2 mL) and aged for 10 min. The solution of precatalyst was added to the flask. The flask was sequentially charged with dried MAO, toluene (3 mL) and 1-hexene (5 mL). After 1 h, the polymerization mixture was poured into acidified ethanol. Polymers were recovered and dried in a vacuum oven at 40 °C.

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Supporting Information Available: Figures showing ^{1}H and ^{13}C NMR spectra of ligand H_2L^1 and H_2L^2, and complexes **2** and **3** and text describing a fractionation experiment and a table giving characterization data of each fraction. This material is available free of charge via the Internet at http://pubs.acs.org.

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