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ARTICLE

Isotactic-Specific Polymerization of Propene by a C_s-Symmetric Zirconium(IV) Complex Bearing a Dianionic Tridentate [$^-$NNN$^-$] Amidomethylpyrrolidepyridine Ligand

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ABSTRACT: The synthesis and characterization of a new tridentate amidomethylpyrrolidepyridine ligand (**LigH$_2$**) and of the corresponding LigZr(NMe$_2$)$_2$ complex (**1**) are described. Characterization of **1** by single-crystal X-ray diffraction analysis showed a slightly distorted square-pyramidal geometry. Variable-temperature NMR analysis suggested that **1** adopts a C_s-symmetric structure in solution. Complex **1** in combination with Al^{i}Bu$_2$H and methylalumoxane afforded a highly active single-site catalyst for the polymerization of ethylene and propene, producing ultrahigh molecular weight linear polyethylene and isotactic polypropylene via an "*enantiomorphic sites*" mechanism of steric control.

Introduction

Nitrogen-based polydentate ligands have proved to be useful alternatives to the cyclopentadienyl ligand for a new generation of homogeneous olefin polymerization catalysts. In this framework, amidinates,[1] pyrrolide-imines,[2] 2,6-bis-(*N*-aryliminomethyl)-pyridines,[3] α-diimines,[4] and 2-aminopyridines[5−8] have attracted particular interest and have been the object of several studies. In this context, we recently reported the synthesis of a new family of bis(amidomethylpyridine) zirconium(IV) complexes, which afforded moderately active catalysts in the polymerization of ethylene and propene producing, in some cases, ultra-high molecular weight isotactic enriched polypropylene.[9]

A particularly promising class of pyridylamido group 4 olefin polymerization catalysts was discovered by researchers at Dow and Symyx, using a high-throughput parallel screening approach. Most of these complexes showed one bidentate ligand coordinated to the metal center and resulted active in propylene polymerization, producing atactic polypropylene. In the presence of an aromatic substituent in the ortho position of the pyridine ring, a metal−carbon σ bond formed by ortho-metalation of the phenyl group, generating a tridentate ligation. The corresponding hafnium complexes showed C_1-symmetric structures and high activity and isospecificity in the polymerization of propylene and in the copolymerization of various vinyl monomers at high temperatures.[10,12] Despite the well-defined nature of the precatalysts, the above complexes exhibited polymerization behavior indicative of multiple catalytic species.[13,14] Theoretical and experimental work by Froese et al. suggested the formation of a highly active catalytic species generated by modification of the ligand structure by insertion of ethylene (or α-olefin) into Hf−aryl bonds, besides the cationic species derived from methyde abstraction by ionizing agents.[13] More recently, Coates et al. observed intramolecular 2,1- insertion into the Hf−CH$_3$ for a pyridylamidohafnium trimethyl complex bearing a vinyl group in the ligand framework. After activation with B(C$_6$F$_5$)$_3$, the modified hafnium complex polymerized propylene to isotactic polypropylene in a living fashion.[15]

Actually, the isospecificity of the pyridylamido catalysts seems to be connected to the ligand structural features, in particular to the bulky substituents on the amido moiety and the tridentate ligation to the metal center.[10i] The presence of a chiral center on the ligand framework seems not to be essential for the observed isospecificity. Coates, in fact, reported C_s-symmetric dimethyl pyridylamidohafnium complexes as catalyst precursors for isoselective propylene and 1-hexene polymerization, even in the absence of a chiral center in the ligand framework.[16]

On this basis, we designed a new class of tridentate amido-pyrrolidepyridine ligands in which tridentate ligation is accomplished by introduction of a pyrrole moiety in the ligand framework (Chart 1).

Herein, we report the synthesis and the characterization of the first dianionic tridentate [$^-$NNN$^-$] ligand of this class, the synthesis of the corresponding bis(dimethylamido)zirconium-(IV) complex, and preliminary results on the polymerization of ethylene and α-olefins.

Results and Discussion

The aminomethylpyrrolidepyridine ligand was synthesized via the Suzuky-Miyaura cross-coupling reaction of 6-bromo-2-pyridine-carboxaldehyde and *N*-Boc-pyrrole-2-boronic acid (Boc = *tert*-butyloxycarbonyl), affording 6-(1*H*-pyrrol-2-yl)pyridine-2-carbaldehyde (**A**) in 60% yield (see Scheme 1).[17,18] A condensation reaction between **A** and 2,6-diisopropylaniline afforded the pyridylimine precursor **B** (93%), which, by reduction with NaBH$_3$CN, gave the pyridylaminopyrrole ligand (**LigH$_2$**) in good yield (98%). Compounds **A** and **B** as well as **LigH$_2$** have been characterized by NMR spectroscopy and elemental analysis.

The bis(dimethylamido)zirconium(IV) complex **1** was prepared by the reaction of **LigH$_2$** and tetrakis(dimethylamido)-zirconium(IV) in a 1:1 ratio in hexane (Scheme 2).

Reaction proceeded cleanly with good yield (87%), producing **1** as a yellow solid, which was fully characterized by NMR

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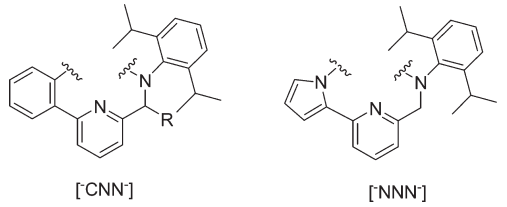
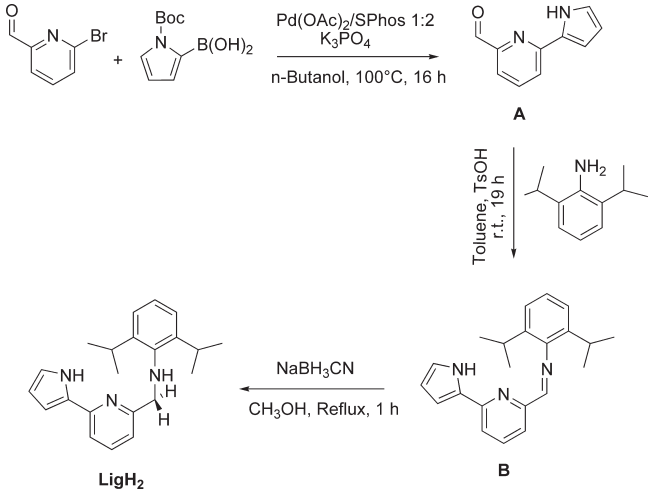
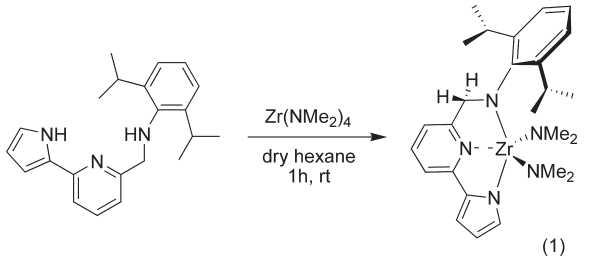
Chart 1



Scheme 1



Scheme 2



spectroscopy, elemental analysis, and X-ray diffraction analysis. Suitable crystals were grown from dichloromethane/hexane at room temperature. The molecular structure of **1** is shown in Figure 1; selected bond distances and angles are listed in Table 1. The molecular structure of **1** is similar to that of analogous pyridylamidohafnium complexes described by Coates et al.[16]

The five-coordinated complex adopts a slightly distorted square-pyramidal geometry, as can be seen by considering N(1), N(2), N(3), and N(4) as the base plane atoms (rmsd 0.170 Å) and N(5) as the apex atom. The Zr(1) atom deviates from the base plane by 0.646(3) Å, while the angle between N(5) atom and the base plane turns out to be of 88.2(3)°. The ratio $\tau = (\beta - \alpha)/60°$, where β and α are respectively the two basal angles N(1)—Zr—N(3) and N(2)—Zr—N(4), represents the fractional distortion from the square-pyramidal (sp) versus the trigonal-bipyramidal (tbp) geometry. A value of zero applies to a compound with a sp geometry and a value of 1 to a tbp geometry; in this case, $\tau = 0.07$. Values close to zero are observed also for the analogous pyridylamido Hf compounds, which can be also described as distorted sp complexes.[10i,16] Moreover, Coates et al. reported that the analogous Hf complex bearing an achiral pyridylamine ligand displays a nearly C_s symmetry in the solid state. In our case, a more pronounced distortion from the idealized C_s symmetry is observed. The N-aryl ring turns out to be significantly canted with respect to the plane defined by Zr(1),

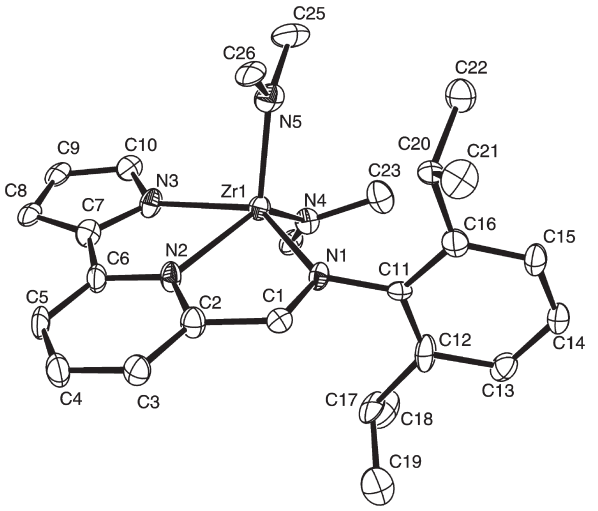


Figure 1. Ortep drawing of the molecular structure of compound **1**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Compound 1

Zr1—N1	2.127(5)	N1—C11	1.424(8)
Zr1—N2	2.302(5)	N2—C2	1.371(8)
Zr1—N3	2.238(5)	N2—C6	1.365(8)
Zr1—N4	2.051(6)	C1—N1	1.464(8)
Zr1—N5	2.061(7)	C1—C2	1.476(9)
Zr1—C23	2.831(8)	C6—C7	1.458(9)
N1—C1	1.463(8)	N3—C7	1.386(9)
N1—Zr1—N2	71.4(2)	N2—Zr1—N4	134.6 (2)
N1—Zr1—N3	138.8(2)	N2—Zr1—N5	112.7(3)
N1—Zr1—N4	108.4(2)	N3—Zr1—N5	100.0(2)
N1—Zr1—N5	105.9(2)	N3—Zr1—N4	91.1 (2)
N2—Zr1—N3	69.2(2)	N4—Zr1—N5	110.8(2)
Zr1—N4—C23	106.0(4)	Zr1—N4—C24	140.7(4)
Zr1—N5—C25	127.8(4)	Zr1—N5—C26	119.9(4)

N(1), N(2), and N(3) atoms, and the displacement of the ipso carbon C(11) is 0.48 Å, while for the pyridylamido Hf compound it is only 0.15 Å.[16]

It is noteworthy that the C(23) atom is at 2.831(8) Å from the Zr(1) atom, and the angle N4—Zr1—C23 turns out to be 106.0(4)°. These values are significantly lower than the corresponding distances and angles observed for the C24, C25, and C26 atoms.[19] This finding could be a diagnostic sign for an agostic interaction.[20]

The ^{1}H NMR spectrum at room temperature showed sharp signals and a pattern compatible with a C_s-symmetric structure in solution, as indicated by the presence of one singlet for the Zr—NMe_2 at 2.76 ppm, one singlet for the two methylenic hydrogen atoms at 4.71 ppm, and two doublets at 1.18 and 1.21 ppm for the isopropyl methyl groups. Variable-temperature NMR studies, performed between 193 to 353 K, did not show any change in the spectra.

Compound **1** was tested as a catalyst for the polymerization of ethylene and higher α-olefins using different activators. Activities, melting temperatures of the polyethylenes, and molecular weight data are collected in Table 2. Compound **1**, in combination with methyaluminoxane (MAO), was inactive (run 4, Table 2). In the presence of $Al^iBu_2H/[HNMe_2Ph][B(C_6F_5)_4]$ as a cocatalyst, complex **1** promoted polymerization of ethylene at room temperature with moderate activity, producing linear polyethylene with narrow molecular weight distribution (PDI = 1.5; run 5, Table 2). Activation by Al^iBu_2H/MAO resulted in a highly active catalytic system, even at room temperature, producing ultrahigh molecular weight polyethylene, having

Table 2. Ethylene Polymerization Results

run[a]	cocatalyst	T [°C]	activity[b]	T_m [°C]	M_w [$\times 10^4$]	M_w/M_n
1	Al^iBu_2H/MAO_d	25	1.84	136.5	185	2.1
2	Al^iBu_2H/MAO_d	50	1.08	135.8	310	2.7
3	Al^iBu_2H/MAO_d	75	0.69	136.2	69	3.0
4	MAO_d	25	trace			
5[c]	$Al^iBu_2H/[HNPhMe_2][B(C_6F_5)_4]$	25	0.18	137.9	89	1.5

[a] Conditions: precatalyst **1** = 2.5 μmol; Al^iBu_2H/Zr = 30; $Al_{(MAO)}/Zr$ = 1000; ethylene pressure = 1 atm; toluene = 100 mL; time = 7 min. Dried MAO_d obtained by distilling off the solvent from the commercial solution. [b] Activity = kg polymer (mmol Zr·h·atm)$^{-1}$. [c] Compound **1** = 10 μmol; Al^iBu_2H/Zr = 30; $[HNPhMe_2]/[B(C_6F_5)_4]$ = 1.1 equiv; ethylene pressure = 1 atm; toluene = 35 mL; time = 7 min.

Table 3. Propylene Polymerization Results

run[a]	cocatalyst	T [°C]	P [atm]	time [h]	activity[b]	[*mmmm*] %	M_w [$\times 10^3$]	M_w/M_n
1[c]	Al^iBu_2H/MAO_d	25	1	3	0.87	52	1.0	1.7
2	Al^iBu_2H/MAO_d	25	6	1	3.96	73	38.8	1.4
3	Al^iBu_2H/MAO_d	50	6	1	1.02	66	26.5	1.6

[a] Conditions: precatalyst **1** = 10 μmol; Al^iBu_2H/Zr = 30; $Al_{(MAO)}/Zr$ = 1000; toluene = 100 mL; dried MAO obtained by distilling off the solvent from the commercial solution. [b] Activity = kg polymer(mol Zr·h·atm)$^{-1}$. [c] Toluene = 35 mL.

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

monomodal and relatively narrow molecular weight distribution (PDI = 2.1; run 1, Table 2). When the temperature was increased, in the presence of the latter activator system, the activity decreased and the molecular weight distributions were larger, but still monomodal (PDI = 2.7 ÷ 3). Such results seem to be indicative of a single-site nature of the active species. On the contrary, the Dow−Symyx complexes exhibited a polymerization behavior indicative of multiple catalytic species.[13,14]

The propylene polymerization behavior of complex **1** activated by Al^iBu_2H/MAO was also studied. Results of propylene polymerization are reported in Table 3. Under 6 atm of propene and at 25 °C, catalyst **1** produced isotactic polypropylene with a narrow molecular weight distribution (PDI = 1.4), clear indication of a single site behavior (run 2, Table 3). Microstructural analysis via ^{13}C NMR spectroscopy revealed that the obtained polymer is mainly regioregular and isotactic ([*mmmm*] = 73%; Figure 2). Analysis of the methyl region revealed a 2:2:1 ratio of the peaks corresponding to [*mmmr*]/[*mmrr*]/[*mrrm*] pentads, as expected for the statistical model of the "*enantiomorphic sites*" mechanism of the stereospecific propagation.[21] Minor resonances at 12.4, 13.5, 28.8, 30.4, 32.3, 33.2, 34.6, and 41.2 ppm were attributed, according to the literature,[10i,22] to isolated regioerrors (3%), arising from head-to-head or tail-to-tail misinsertions. In the Fisher projection, the vicinal methyls of the regioinverted units can show either *erythro* or *threo* configuration. In our case, the exclusive presence of signals attributed to isolated regioinverted units with vicinal methyls in *threo* configuration was observed.

The latter observation indicates that primary (1,2) and secondary (2,1) insertion of the monomer occur with the same enantioface selectivity,[23] differently from the behavior observed for isotactic specific metallocene polymerization catalysts.[21d,c] The same microstructure was observed by Busico et al. for the isotactic polypropylene obtained in the presence of C_1-symmetric Hf pyridyl-amido catalysts[10i] and by some of us for the isotactic polypropylene obtained in the presence of a titanium(IV) catalyst bearing the (*E*)-2-*tert*-butyl-6[(quinoline-8-ylimino)methyl]phenolate) ligand.[22]

In the ^{13}C NMR spectrum of the polypropylene sample obtained in run 2 Table 3, in addition to the main resonances, signals attributable to the isobutyl end groups and to the *n*-propyl end groups in a 2:1 ratio were also observed. (See Figures 2 and 3.) The isobutyl end groups could arise from primary propylene insertion into Zr−Me or Zr−*i*-Bu bonds in the initiation step or from the hydrolysis of zirconium- or aluminum-bound primary growing chains in the termination step. The chemical shift of the isobutyl end groups is sensitive to the stereochemistry of the neighboring propene units. The two methyl groups of isobutyl end groups are not equivalent because they occupy the "*erythro*-like" and "*threo*-like" position with respect to the neighboring methyl groups and, thus, in the ^{13}C NMR, give rise to two signals around 20 and 22 ppm, respectively. In addition, each signal could split into four peaks, depending on the configuration of methyl groups of the neighboring three propene units (*mm*, *mr*, *rm*, *rr*). The expanded spectrum of the isobutyl chain end region is shown in Figure 3, and the different resonances observed for the diastereotopic methyls of the isobutyl end groups have been assigned according to the literature.[24] The intensity of the signals due to methyl groups in the *mm* configuration in comparison with the same methyl groups in the *rr* configuration shows that primary propene insertion is predominantly isotactic specific.

The *n*-propyl end groups, instead, could arise from primary propene insertion into Zr−hydrogen bonds. The formation of Zr−H bonds deriving from β-hydrogen elimination has to be disregarded in view of the negligible intensity of the resonances of unsaturated chain end groups. Reasonably, the Zr−hydrogen bonds could come from the reaction between the precatalyst **1**

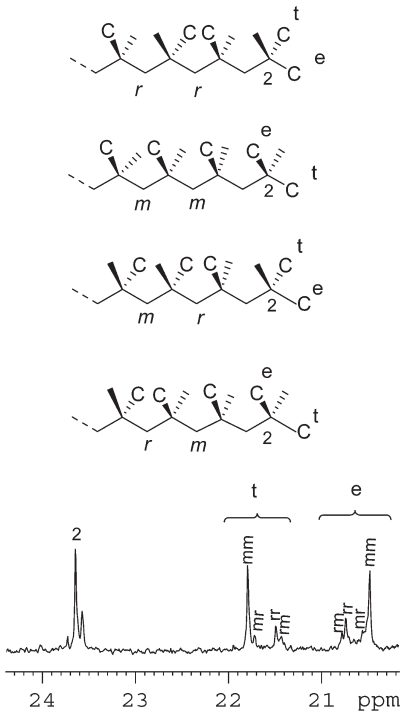


Figure 3. The isobutyl chain end region of the ^{13}C NMR spectrum (1,1,2,2-tetrachloroethane-d_2, 100 °C) of i-PP produced in run 2, Table 3. δ in parts per million from hexamethyldisiloxane.

and Al^{i}Bu$_2$H, as previously observed for the rac-[ethylen-1,2-bis-(1-indenyl)zirconium(IV)bis(dimethylamido)] complex, which, in combination with Al^{i}Bu$_2$H, produced the zirconium hydride complex.[25] The *n*-propyl end groups could also come from the termination step by the hydrolysis of secondary growing chains, formed after regioerrors (2,1 insertion of propylene into Zr-primary growing chain bonds). The latter hypothesis was ruled out by a deuterium labeling experiment performed by adding a 1:1 mixture of CF_3COOD and CH_3CH_2OD to terminate a polymerization run. ^2H NMR analysis of the obtained polypropylene showed the exclusive presence of $CH_2DCH(CH_3)CH_2-$ end groups, deriving from deuteriolysis of the primary polymer chain bound to either Zr or Al (Figure 4). Therefore, the *n*-propyl end groups arise only from the initiation step. This is further confirmed by the observation that the analogous dibenzyl zirconium(IV) complex, in combination with $[Ph_3C]^+[B(C_6F_5)_4]^-$ alone, produced isotactic polypropylene without *n*-propyl end groups.[26] As observed above for isobutyl end groups, the chemical shift of the *n*-propyl end group is also sensitive to the stereochemistry of the neighboring propene units.[27] In our case, the *n*-propyl end groups were adjacent to an isotactic *mm* stereochemical triad, indication that primary propene insertion is isotactic specific.

By increasing the polymerization temperature from 25 to 50 °C, the **1**/Al^{i}Bu$_2$H/MAO catalytic system was still active in the polymerization of propylene. At 50 °C, the activity, the tacticity ([*mmmm*] = 66%), and the molecular weight of the obtained polypropylene decreased. By the way, gel permeation chromatography (GPC) analysis revealed narrow molecular weight distribution (PDI = 1.6), an indication that the single-site catalytic species is still present in solution (run 3, Table 3). Apart from the different degree of isotacticity, the obtained polypropylene showed a ^{13}C NMR spectrum very similar to that observed for the polymer obtained at room temperature.

The complex was also tested in 1-hexene polymerization. Complex **1**, activated with Al^{i}Bu$_2$H/MAO, was moderately active in polymerization, producing poly(1-hexene), which possessed,

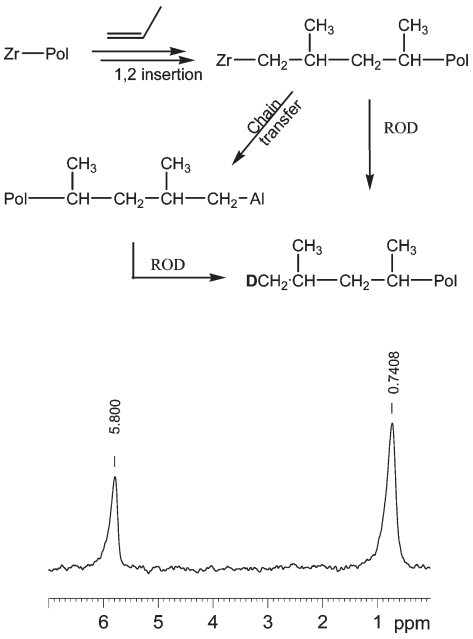


Figure 4. ^2H NMR spectrum (1,1,2,2-tetrachloroethane-d_2, 100 °C) of polypropylene produced in the presence of catalytic system **1**/Al^{i}Bu$_2$H/MAO. Polymerization run was terminated by injecting a 1:1 mixture of CF_3COOD and CH_3CH_2OD. δ in parts per million from hexamethyldisiloxane.

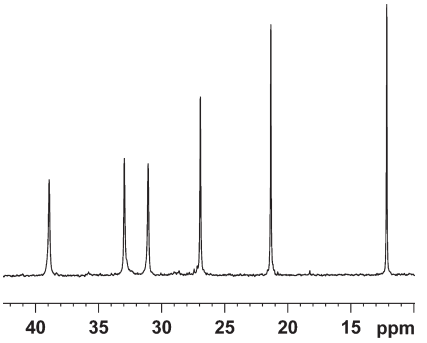


Figure 5. ^{13}C NMR spectrum (1,1,2,2-tetrachloroethane-d_2, 100 °C) of poly(1-hexene) produced in the presence of catalytic system **1**/Al^{i}Bu$_2$H/MAO. δ in parts per million from hexamethyldisiloxane.

however, a narrow molecular weight distribution (PDI = 1.2). Analysis of the poly(1-hexene) microstructure via ^{13}C NMR spectroscopy revealed that the polymer was regioregular and almost perfectly isotactic ([*mmmm*] > 99%); resonances attributable to stereoerrors and to end groups were not observed (Figure 5). It is worth noting that the increase of enantioface selectivity in the polymerization of higher α-olefins with respect to propylene has been previously observed for isospecific propene polymerization catalysts, such as C_2- and C_1-symmetric zirconocenes[28] and for aspecific propene polymerization catalysts, such as the binaphthyl-bridged salen zirconium catalyst[29] and bis-(aminomethylpyridinato) zirconium(IV) complexes.[9]

Conclusion

The understanding of the correlations between catalyst structure and stereoselectivity of polymerization is one of the most fascinating issues in olefin polymerization catalysis. The variety of electronic and steric parameters that can be modulated in the case of nonmetallocene catalysts results often in unexpected, unpredictable stereospecificity.[30]

The new synthesized zirconium(IV) complex bearing the amidomethylpyrrolidepyridine ligand showed a slightly distorted

square-pyramidal geometry in the solid state and "time averaged" C_s-symmetric structure in solution. Despite the precatalyst structure, isotactic polyolefins with narrow molecular weight distributions were produced. ^{13}C NMR microstructural analysis of polypropylene suggested that the isospecifity results from the "*enantiomorphic sites*" mechanism of steric control.

C_s-symmetric catalyst precursors which act as isospecific catalysts via "enantiomorphic sites" control are rare,[16] and to explain their polymerization behavior on the basis of the generally accepted symmetry rules is complicated.[21c,21d] Coates et al. explained the unexpected isoselectivity for C_s-symmetric pyridylamidohafnium catalysts hypothesizing in situ ligand modification due to insertion of propylene into the Hf−aryl bond.[16] Reasonably, in our case, ligand modification as a consequence of the insertion of one monomer unit into a Zr−pyrrolyl bond is unlikely, while other ligand modification cannot be excluded. For instance, Schrock et al. reported CH bond activation of the ortho methyl group in the mesityl substituent of the cationic triamido zirconium(IV) complex.[31]

Alternatively, the observed feature could be related to a loss of symmetry of the cationic active species as a consequence of a higher hapticity of the pyrrole moiety, as suggested by a reviewer. As a matter of fact, penta-hapto coordination of pyrrolyl ligands in zirconium complexes has been observed previously.[32]

However, even without any ligand modification, the unexpected isoselectivity observed for **1** could be related to the square-pyramidal coordination geometry observed in the solid state. For instance, the cationic active species could prefer a sp coordination geometry, for example, with the NNN tridentate ligand and the coordinated olefin laying in the plane and the growing chain occupying the apical position. Experimental and theoretical investigations are currently in progress in order to address this issue, as well as to develop a family of catalysts based on ligands of this class.

Experimental Section

General Procedure. Manipulation of sensitive materials was carried out under nitrogen using Schlenk or glovebox techniques. Hexane, benzene, and toluene were refluxed over sodium/benzophenone and methylene chloride over calcium hydride, then distilled under nitrogen prior to use. $CDCl_3$, CD_2Cl_2, and C_6D_6 were dried over calcium hydride, distilled prior to use, and stored on molecular sieves. 1,1,2,2-tetrachloroethane-d_2 was used as received. MAO (10 wt %) in toluene solution was purchased from Sigma-Aldrich; the residual $AlMe_3$ contained in it was removed by distilling the volatile under reduced pressure, washing the resulting solid with dry hexane, and drying the obtained white powder in vacuo (MAO_d). Reagents were purchased from Sigma-Aldrich and used as received. Ethylene and propene were purchased from SON and used without further purification; 1-hexene was distilled over calcium hydride prior to use. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer (^1H, 400 MHz; ^{13}C, 100 MHz). ^{13}C NMR polymer spectra were recorded on a Bruker AM-250 spectrometer (^{13}C at 62.5 MHz) in 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$) at 100 °C and reported relative to hexamethyldisiloxane. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 series C,H,N,S Analyzer.

Molecular weights (M_n and M_w) and polydispersities (M_w/M_n) of polyethylene and polypropylene were determined by high-temperature GPC using a Waters GPC-V200 RI detector. The measurements were recorded at 135 °C using 1,2-dichlorobenzene as a solvent and Styragel columns (range 10^7 to 10^3). The molecular weight and the molar mass distribution of the poly-1-hexene sample were measured by GPC at 30 °C, using $CHCl_3$ as a solvent, a flow rate of the eluant of 1 mL/min, and narrow polystyrene standards as a reference. The measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four Styragel columns (range 1000−1 000 000 Å). Every value was the average of two independent measurements.

Polymer melting points (T_m) were measured by differential scanning calorimetry using a TA Instruments DSC 2920 in a nitrogen flow with a heating and cooling rate of 10 °C min^{-1}. Melting temperatures were reported for the second heating cycle.

Synthesis of 6-(1*H*-Pyrrol-2-yl)pyridine-2-carbaldehyde (A). Palladium(II)acetate (50 mg, 0.2 mmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (0.186 g, 0.4 mmol), *N*-(*t*-butoxycarbonyl)-pyrrole-2-boronic acid (1.0 g, 4.74 mmol), 6-bromo-2-pyridine-carboxaldehyde (0.588 g, 3.16 mmol), and K_3PO_4 (2.233 g, 10.5 mmol) were mixed in 12 mL of *n*-butanol; the resulting mixture was heated to 100 °C and stirred for 16 h. The reaction mixture was allowed to cool to room temperature, then was filtered through a thin pad of silica gel, eluting with ethyl acetate. The solvent was distilled off by rotary evaporation. The crude product was purified via flash column chromatography on silica gel using 9:1 hexane/ethyl acetate as the eluent, obtaining the product (**A**) as pale yellow solid (0.305 g, 57%). ^1H NMR ($CDCl_3$; 293 K): δ 6.32 (1H, m, $-NC_4H_3$), 6.78 (1H, m, $-NC_4H_3$), 6.98 (1H, m, $-NC_4H_3$), 7.68−7.80 (3H, m, Py−H), 10.05 (1H, s, −COH). ^{13}C NMR ($CDCl_3$; 293 K): δ 108.58, 110.87, 118.81, 120.92, 122.41, 137.6 (Ar−*C*), 193.87 (COH). Anal. Calcd for $C_{10}H_8N_2O$ (172.18): C, 69.76; H, 4.68; N, 16.27. Found C, 69.75; H, 4.57; N, 15.98.

Synthesis of (*E*)-*N*-((6-(1*H*-Pyrrol-2-yl)pyridin-2-yl)methylene)-2,6-diisopropylbenzenamine (B). To a solution of 6-(1*H*-pyrrol-2-yl)pyridine-2-carbaldehyde (0.273 g, 1.6 mmol) in toluene (30 mL) containing 3 Å molecular sieves were added 2,6-diisopropylaniline (0.302 g, 1.7 mmol) and *p*-toluenesulfonic acid (20 mg, 0.1 mmol) at room temperature. The resulting mixture was refluxed for 19 h, then cooled to room temperature and filtered. The solvent was distilled off by rotary evaporation. The crude product was crystallized from toluene, obtaining a red solid (0.499 g, yield 93%). ^1H NMR ($CDCl_3$; 293 K): δ 1.18 (12H, d, $-CH(CH_3)_2$), 2.95 (2H, m, $-CH(CH_3)_2$), 6.31 (1H, m, $-NC_4H_3$), 6.75 (1H, m, $-NC_4H_3$), 6.93 (1H, m, $-NC_4H_3$), 7.02−7.18 (3H, m, *i*-$Pr_2C_6H_3$), 7.63 (1H, d, Py−H), 7.80 (1H, t, Py−H), 7.99 (1H, d, Py−H), 8.27 (1H, s, −CH=N). ^{13}C NMR ($CDCl_3$; 293 K): δ 23.68 ($CH(CH_3)_2$), 28.16 ($CH(CH_3)_2$), 107.98, 110.60, 118.60, 119.93, 122.97, 123.27, 124.67, 126.48, 126.82, 137.40, 141.29, 143.62 (Ar−C), 163.46 (CH=N). Anal. Calcd for $C_{22}H_{27}N_3$ (331.45): C, 79.72; H, 7.60; N, 12.68. Found C, 79.49; H, 7.53; N, 12.45.

Synthesis of $LigH_2$. Reduction of the imine functionality was carried out on (*E*)-*N*-((6-(1*H*-pyrrol-2-yl)pyridin-2-yl)methylene)-2,6-diisopropylbenzenamine (0.499 g; 1.5 mmol) by using $NaBH_3CN$ (0.132 g 2.1 mmol) in methanol, following a previously reported procedure,[9] obtaining **$LigH_2$** as a light yellow powder (yield 98%). ^1H NMR ($CDCl_3$; 293 K): δ 1.27 (12H, d, $-CH(CH_3)_2$), 3.40 (2H, m, $-CH(CH_3)_2$), 4.18 (2H, br s, CH_2Py), 6.32 (1H, m, $-NC_4H_3$), 6.74 (1H, m, $-NC_4H_3$), 6.93 (1H, m, $-NC_4H_3$), 7.03 (1H, d, Py−H), 7.05−7.15 (3H, m, *i*-$Pr_2C_6H_3$), 7.45 (1H, d, Py−H), 7.60 (1H, t, Py−H). ^{13}C NMR ($CDCl_3$; 293 K): δ 24.40 ($CH(CH_3)_2$), 28.03 ($CH(CH_3)_2$), 56.78 ($PyCH_2$), 107.45, 110.56, 119.87 (NC_4H_3), 116.73, 118.85, 137.28 (*i*-$Pr_2C_6H_3$), 122.98, 123.82, 124.00 (Py−C), 131.73, 132.66, 142.62, 143.62, 150.19, 158.12 (Ar−C). Anal. Calcd for $C_{22}H_{27}N_3$ (333.47): C, 79.24; H, 8.18; N, 12.60. Found C, 79.15; H, 8.04; N, 12.38.

Synthesis of Complex (1). $LigH_2$ (0.168 g, 0.5 mmol) and tetrakis(dimethylamido)zirconium (0.125 g, 0.47 mmol) were dissolved in 15 mL of dry hexane. The solution was stirred for 1 h at room temperature. The solvent was distilled off in vacuo and the resulting powder washed with dry hexane (2 × 5 mL). The product was crystallized from dichloromethane/hexane. Suitable crystals for X-ray analysis were grown from dichloromehane/hexane at room temperature (0.210 g, 87% yield).

^{1}H NMR (C_6D_6; 293 K): δ 1.18 (6H, d, $-CH(CH_3)_2$), 1.21 (6H, d, $-CH(CH_3)_2$), 2.76 (12H, br s, $-N(CH_3)_2$), 3.51 (2H, m, $-CH(CH_3)_2$), 4.71 (2H, br s, Py$-CH_2$), 6.19 (1H, d, $-NC_4H_3$), 6.65 (1H, m, $-NC_4H_3$), 6.88 (1H, d, $-NC_4H_3$), 6.89−6.94 (2H, m, PyH), 7.17−7.20 (3H, m, Ar−H *i*-$Pr_2C_6H_3$), 7.34 (1H, m, PyH). ^{13}C NMR (C_6D_6; 293 K): δ 24.55, 26.97 ($-CH(CH_3)_2$), 28.45 ($-CH(CH_3)_2$), 41.18 ($N(CH_3)_2$), 66.24 ($-PyCH_2$), 110.94, 112.98, 113.51, 114.08, 124.14, 125.46, 133.74, 140.20, 140.83, 146.68, 148.94, 155.96, 163.86 (Ar−*C*). Anal. Calcd for $C_{26}H_{37}N_5Zr$ (510.829): C, 61.13; H, 7.30; N, 13.71. Found C, 60.99; H, 7.18; N, 13.68.

Ethylene and Propene Polymerization Procedure. The polymerizations were performed in a magnetically stirred reactor (250 cm^3) or in a 500 mL Büchi glass autoclave. The reactor vessels were charged sequentially with MAO and a toluene solution of compound **1** in toluene (2 mL), preaged for 10 min with a solution of Al*i*Bu_2H in toluene. The mixture was thermostated at the required temperature, and the monomer gas feed was started. After the required polymerization time, the mixture was poured into acidified ethanol. The polymers were recovered by filtration and dried at 40 °C in a vacuum oven.

1-Hexene Polymerization. Polymerization was performed in a magnetically stirred reactor (50 °C) that was charged sequentially with dried MAO (5 mmol), 3 mL of toluene, and 5 mL of 1-hexene. Then, a solution of complex **1** (5 μmol) in toluene (2 mL) preaged for 10 min with a solution of Al^iBu_2H in toluene (0.54 mL, 0.28 M) was added. After 1 h, the polymerization mixture was poured into acidified ethanol. Polymer was recovered and dried in a vacuum oven (yield = 0.130 g). ^{13}C NMR analysis showed [*mmmm*] = 100%. GPC data: $M_w/M_n = 1.2$, $M_n = 85\,300$.

X-Ray Crystallography. Suitable crystals of compound **1** were selected and mounted on a cryoloop with paratone oil and measured at 100 K with a Rigaku AFC7S diffractometer equipped with a Mercury^2 CCD detector using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Data reduction was performed with the crystallographic package CrystalClear.[33] Data have been corrected for Lorentz, polarization, and absorption. The structure was solved by direct methods using the program SIR97[34] and refined by means of full matrix least-squares based on F^2 using the program SHELXL97.[35]

All non-hydrogen atoms were refined anisotropically; hydrogen atoms were positioned geometrically and were included in structure factors calculations but were not refined. A total of 289 refinable parameters were finally considered. Maximum and minimum residual density were respectively +0.54 and −0.57 e Å^{-3}; final disagreement indices: $R = 0.084$ for 2849 reflections with $I > 2\sigma_I$, wR2 = 0.228 for 6189 reflections. The program ORTEP32 has been used for drawing the ORTEP plot.[36]

Crystallographic Data. Formula, $ZrN_5C_{26}H_{37}N_5$; fw = 510.83; system, monoclinic; space group $C2/c$; $Z = 8$; $a = 18.750(5)$ Å; $b = 14.075(4)$ Å; $c = 19.824(5)$ Å; $\beta = 2.766(7)°$; $V = 5226(2)$ Å^3; $D_x = 1.299$ g cm^{-3}; $\mu_{calcd} = 0.44$ mm^{-1}.

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Supporting Information Available: X-ray crystallographic information files in CIF format are available for compound **1.** ^{1}H and ^{13}C NMR spectra of **LigH$_2$** and complex **1**, ^{13}C NMR spectra of polyhexene and polypropylene samples are also available. This material is available free of charge via Internet at http://pubs.acs.org.

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