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Article

Syntheses, Characterization, and Ethylene Polymerization of Half-Sandwich Zirconium Complexes with Tridentate Imino−Quinolinol Ligands

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A series of half-sandwich zirconium complexes with imino-quinolinol ligands have been synthesized and characterized. The catalytic behaviors of these complexes toward ethylene polymerization were investigated in the presence of methylaluminoxane (MAO) as a cocatalyst. The catalytic behaviors were highly affected by the substituent in both cyclopentadienyl and imino−quinolinol ligands. The Cp analogue complexes CpZr[ONN^R]Cl$_2$ (**1a**−**e**) exhibited high activities up to 1.34×10^7 g of PE (mol of Zr)$^{-1}$ h^{-1}, whereas the Cp* analogue complexes Cp*Zr[ONN^R]Cl$_2$ (**2a**−**e**) also showed moderate activities for ethylene polymerization.

The search for new olefin polymerization catalysts based on transition-metal complexes is a field of major interest, involving many academic and industrial research groups. Nonbridged half-sandwich metal complexes have been considered as some of the most robust and effective precatalysts for ethylene polymerization.[1−4] These types of complexes exhibit unique characteristics for the production of novel polymers that are not prepared by conventional Ziegler−Natta catalysts,[5] as well as by ordinary metallocene type[6] and "constrained geometry" half-sandwich metal catalysts (CGC catalysts).[7] The catalytic behavior of these precatalysts and the properties of the resultant polyolefin could be fine-tuned by modifying the substituents of the complex ligands. Over the past decade, there have been numerous reports about this research field,[2,8−10] and we also have reported a series of half-metallocene transition-metal complexes containing bidentate[11] or tridentate[12] ligands exhibiting notable catalytic activities for olefin polymerization.

Commercially, it is of further interest if these catalysts can be procured in as few steps as possible, from "nonexotic" starting materials.[4] Herein, we report a series of half-sandwich zirconium complexes with tridentate imino−quinolinol ligands which are obtained by easy synthetic routes (Scheme 1). Moreover, these half-zirconocene complexes can be simply modified by replacement of the cyclopentadienyl fragment or monoanionic ancillary ligands. The title catalysts activated with methylaluminoxane (MAO) showed high activities in ethylene polymerization.

Results and Discussion

Synthesis and Characterization of the Half-Sandwich Zirconium Complexes. 8-Hydroxy-2-quinolinecarbaldehyde was prepared according to the literature procedure.[13] The imino−quinolinol derivatives **La**−**d** were prepared by condensation reactions of

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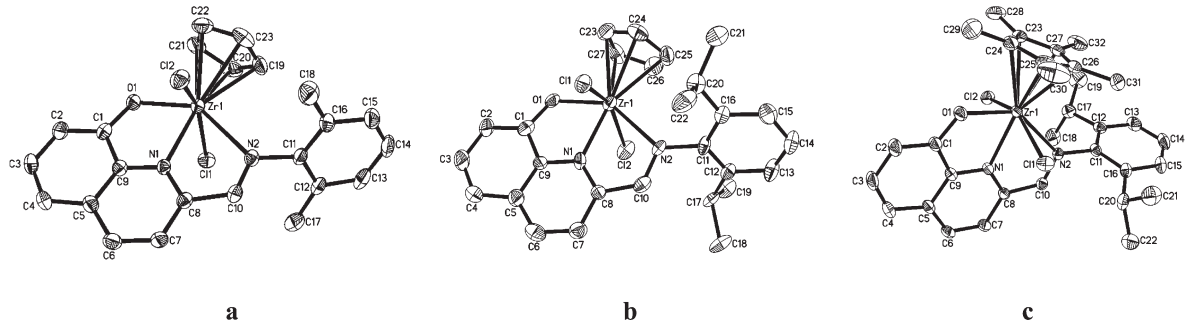
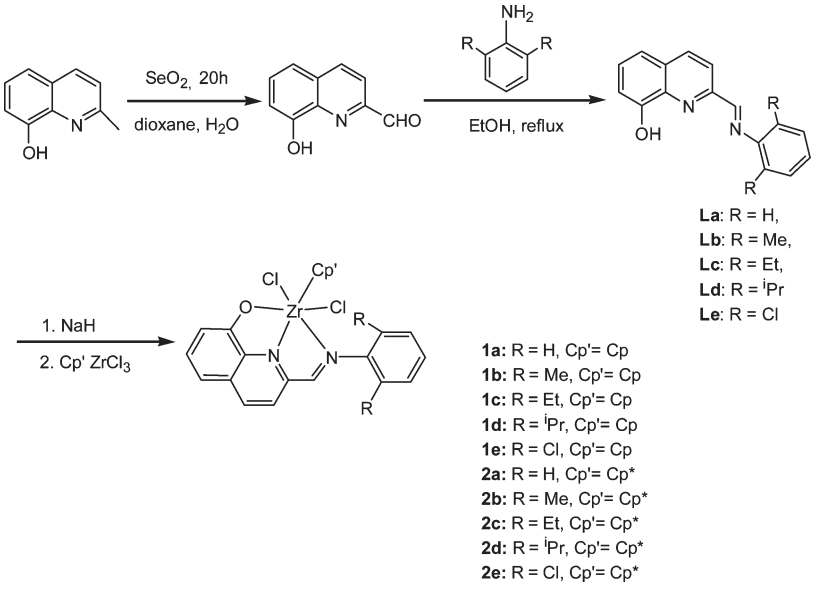


a **b** **c**

Figure 1. ORTEP views of the molecular structures of (a) **1b**, (b) **1d**, and (c) **2d** (H atoms are omitted for clarity). Selected bond distances (Å) and angles (deg) are as follows. For **1b**: Zr(1)−N(1) = 2.267(3), Zr(1)−N(2) = 2.479(3), Zr(1)−O(1) = 2.063(3), Zr(1)−Cl(1) = 2.5234(14), Zr(1)−Cl(2) = 2.5004(14); Cl(2)−Zr(1)−Cl(1) = 153.03(4);. For **1d**: Zr(1)−N(1) = 2.235(6), Zr(1)−N(2) = 2.487(6), Zr(1)−O(1) = 2.048(5), Zr(1)−Cl(1) = 2.522(2), Zr(1)−Cl(2) = 2.490(2); Cl(2)−Zr(1)−Cl(1) = 151.78(7). For **2d**: Zr(1)−N(1) = 2.300(2), Zr(1)−N(2) = 2.603(2), Zr(1)−O(1) = 2.067(2), Zr(1)−Cl(1) = 2.4980(9), Zr(1)−Cl(2) = 2.5043(8); Cl(2)−Zr(1)−Cl(1) = 149.48(3).

Scheme 1. Synthesis of Complexes 1a−e and 2a−e



the 8-hydroxy-2-quinolinecarbaldehyde and corresponding substituent anilines in refluxing ethanol in good yields. When the substituent of aniline is an electron-withdrawing group, a small amount of acid is necessary. **Le** was prepared by reaction of 8-hydroxy-2-quinolinecarbaldehyde and 2,6-dichlorophenylamine in the presence of a few drops of methanoic acid.

Organic ligands were characterized by ^{1}H NMR analyses. By deprotonation of the ligands with excess NaH in THF, the sodium salts were obtained and reacted further with $CpZrCl_3$ or Cp^*ZrCl_3, affording complexes **1a**−**e** and **2a**−**e** (Scheme 1) in good yields.

All the complexes have been fully characterized by elemental and NMR analyses (see the Experimental Section). On comparison of the ^{1}H NMR spectra, the peak of **Lb** at 8.18 ppm (ascribed to the hydroxy proton) disappeared for complex **1b,** indicating the obvious coordination of the oxygen atom to the metal center. The ^{1}H NMR spectra of Zr complexes **1a**−**d and 2a**−**d** show CH═N protons, which are shifted downfield approximately 0.1−0.04 ppm compared to those of the corresponding free ligands, indicating the formation of a Zr−N bond.

Crystals of **1b** suitable for single-crystal X-ray diffraction analysis have been obtained by slow diffusion of hexane into a CH_2Cl_2 solution of compond **1b**. Crystals of **1d** suitable for single-crystal X-ray diffraction analysis were grown by slow diffusion of hexane into a toluene solution. Crystals of **2d** have been obtained by slow diffusion of pentane into a toluene solution at low temperature (−20 °C). Their molecular structures and selected bond lengths and angles are depicted in Figure 1. Crystallographic data and processing parameters are given in the Supporting Information.

The molecular geometries of **1b**,**d** and **2d** are quite similar. If the centroid of the cyclopentadienyl ring is considered as a single coordination site, the zirconium center has a distorted-octahedral coordination with the same arrangement of trans chloride atoms (Cl−Zr−Cl = 153.03(4), 151.78(7), 149.48(3)°). The zirconium atom in complexes **1b,d** and **2d** is six-coordinate, with two nitrogen atoms, one oxygen atom, two chlorine atoms, and a cyclopentadienyl (or pentamethylcyclopentadienyl) ring. The cyclopentadienyl (or pentamethylcyclopentadienyl) group is coordinated at the axial position. The Zr−N bond distances in the Cp analogues **1b**,**d** are shorter

Table 1. Ethylene Polymerization Results with Zirconium Complex 1d/MAO[a]

entry	*P* (atm)	Al/Zr ratio	temp (°C)	activity[b]	$10^{-4}M_v$[c]
1	1	1000	30	28.8	18.3
2	1	2000	30	31.7	17.7
3	1	3000	30	33.2	16.8
4	1	3500	30	20	16.3
5	1	4000	30	15.6	15.9
6	1	3000	50	64.8	13.2
7	1	3000	80	196	10.7
8	1	3000	100	152	7.2
9	6	3000	80	2880	19.6
10	10	3000	80	8177	26.9
11[d]	10	3000	80	8760	20.1
12[e]	10	3000	80	13440	13.8
13[f]	10	3000	80	13200	8.1
14[g]	10	3000	80	7200	27.0
15[h]	10	3000	80	5130	27.1

[a] Conditions: [Zr] 2.5 μmol, toluene (total volume 50 mL), 30 min. [b] Activity in kg of PE (mol of Zr)$^{-1}$ h^{-1}. [c] M_v measured by the Ubbelohde calibrated viscosimeter technique. [d] Time 20 min. [e] Time 10 min. [f] Time 5 min. [g] Time 40 min. [h] Time 60 min.

than in the Cp* analogue **2d**. The Zr(1)−O(1) bond lengths of complexes **1b**,**d** and **2d** (2.063(3), 2.048(5), 2.067(2) Å) are slightly longer than that of structurally related mono-Cp zirconium complexes (1.954−2.040 Å).[14]

Ethylene Polymerization. The complexes **1a**−**e** and **2a**−**e** can be used as catalysts for ethylene polymerization in the presence of MAO as a cocatalyst in toluene. Due to better performance observed by the precatalyst containing an *o*-isopropyl substituent, the precatalyst **1d** was investigated in detail by changing the reaction parameters such as Al/Zr ratio, temperature, and ethylene pressure. The polymerization results are depicted in Table 1.

We began our studies by searching for the optimal Al/Zr ratio. The activity data in Table 1 indicate that the optimal Al/Zr ratio was 3000 (entry 3, Table 1). Increasing the Al/Ti molar ratio from 1000 to 3000 led to higher activity in ethylene polymerization and lower molecular weight (M_v) of the polymer (entries 1−3, Table 1). However, when the Al/Zr ratio was increased to 3500 or 4000, the catalytic activity decreased (entries 4 and 5, Table 1). According to the literature,[15] the active species were probably suppressed by excess MAO; moreover, the amount of $AlMe_3$ contained in MAO led to deactivation of the catalytic centers.

Using 3000/1 as the optimum Al/Zr ratio, we next investigated the effect of temperature on activity and molecular weight (M_v) of the resulting polymers (entries 3 and 6−8, Table 1). In the metallocene system, the optimal polymerization temperature for each system depends on the balance between the propagation rate and the thermal instability.[16] At 1 atm of ethylene at an Al/Zr molar ratio of 3000, the highest activity was observed at 80 °C and slightly decreased at 100 °C (entries 7 and 8, Table 1). The results indicate that the ligands with imino−quinolinol backbones play an important role in stabilizing the active species at high temperature. However, the molecular weights of polyethylene decrease with elevating temperature due to a faster chain transfer and termination at higher temperature.

Table 2. Ethylene Polymerization Results with Zirconium Complexes 1a−e/MAO and 2a−2e/MAO[a]

entry	procat.	amt of PE (g)	activity[b]	$10^{-4}M_v$[c]
1	**1a**	3.4	2755	12.3
2	**1b**	4.8	3911	20.5
3	**1c**	7.1	5680	22.8
4	**1d**	10.2	8177	26.9
5	**1e**	1.4	1155	17.3
6	**2a**	0.6	497	7.6
7	**2b**	1.2	977	13.6
8	**2c**	1.5	1200	16.4
9	**2d**	2.2	1777	19.7
10	**2e**	0.3	266	11.5

[a] Conditions: 2.5 μmol of procatalyst; 10 atm of ethylene; Al/Zr = 3000; 80 °C; 30 min; toluene (total volume 50 mL). [b] Activity in kg of PE (mol of Zr)$^{-1}$ h^{-1}. [c] M_v measured by the Ubbelohde calibrated viscosimeter technique.

When the ethylene pressure was increased, the catalytic activity generally notably improved.[17] When the ethylene pressure was increased from 1 to 10 atm, the polymerization activity further increased to 8.17×10^6 g of PE (mol of Zr)$^{-1}$ h^{-1} in the current catalytic system (entry 10, Table 1). The polyethylene obtained under high ethylene pressure usually exhibits high M_v values (entries 7, 9, and 10, Table 1).

To determine the effect of reaction time on the activity and molecular weight (M_v) of the resulting polymers, the ethylene polymerization was conducted over different time periods, namely, 5, 10, 20, 30, 40, and 60 min (entries 10−15, Table 1); the highest activity (1.34×10^7 g of PE (mol of Zr)$^{-1}$ h^{-1}) was obtained in a period of 10 min.

Ethylene polymerizations by the title complexes Cp′Zr-[ONN^R]Cl$_2$ (**1a**−**e** and **2a**−**e**) in the presence of MAO were examined to explore the effect of substituents on both the cyclopentadienyl and the imino−quinolinol ligands with an Al/Zr molar ratio of 3000 at 80 °C under 10 atm of ethylene, and the results are summarized in Table 2.

The nature of the R group on the ligand has a significant effect on the catalytic activity and M_v value for the resultant polymer. There are observable effects of the ligand environment, and the activities of complexes decrease in the order **1d** (R = ^{i}Pr) > **1c** (R = Et) > **1b** (R = Me) > **1a** (R = H) > **1e** (R = Cl) and **2d** (R = ^{i}Pr) > **2c** (R = Et) > **2b** (R = Me) > **2a** (R = H) > **2e** (R = Cl). The ^{i}Pr-substituted derivatives showed the highest activities (entries 4 and 9, Table 2). The steric hindrance caused by ortho substituents of imino−aryl rings protects the active species and results in high activity, as seen previously.[18] On the other hand, the ^{i}Pr-substituted derivative **1d** has a better solubility, and its active species are better stabilized, resulting in a higher activity.[15,19] The Cl-substituted derivatives showed the lowest activities (entries 5 and 10, Table 2). These results clearly demonstrate that bulky and donating substituents on the ligands in the ortho position seem to be important for high

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catalytic activity. In addition, the activities of the complexes $CpZr[ONN^R]Cl_2$ are much higher than those of the complexes $Cp^*Zr[ONN^R]Cl_2$ suggesting that substituents on the cyclopentadienyl ligand also affect the catalytic activity. Moreover, the M_v values using the Cp analogues (**1a**−**e**) were higher than those for the Cp* analogues (**2a**−**e**).

Conclusions

In summary, a series of half-sandwich zirconium complexes containing a monoanionic tridentate [ONN] ligand have been synthesized and characterized. A combination of X-ray crystallographic and spectroscopic studies confirmed the structure of these half-zirconocene complexes. On activation with excessive amounts of MAO, these half-sandwich zirconium complexes exhibit high catalytic activities toward ethylene polymerization. Remarkably, these zirconium precatalysts exhibited excellent thermal stability at 80 °C, with regard to industrial requirements.

Experimental Section

General Considerations. All operations were carried out under a pure argon atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF), hexane, pentane, and toluene were distilled from sodium−benzophenone. Dichloromethane was distilled from calcium hydride. Commercial reagents, namely, NaH (60%), $CpZrCl_3$, Cp^*ZrCl_3, methylaluminoxane (MAO, 1.46 M in toluene), 2-methyl-quinolin-8-ol, and SeO_2, were purchased from Acros Co. 8-Hydroxyquinoline-2-carbaldehyde was prepared according to the literature procedure.[13]

^{1}H (400 MHz) NMR measurements were obtained on a Bruker AC 400 spectrometer in $CDCl_3$ solution. Elemental analyses for C, N, and H were carried out on an Elementar III Vario EI analyzer.

$[ONN^H]H_2$ (La). A mixture of 8-hydroxy-2-quinolinecarbaldehyde (0.6 g, 3.5 mmol) and 30 mL of ethanol was heated to 80 °C, and then a solution of phenylamine (0.38 g, 3.5 mmol) in 30 mL of ethanol was added dropwise. The reaction mixture was refluxed for 6 h and cooled to room temperature. Purification by column chromatography used 1/3 dichloromethane/ petroleum ether (1% triethylamine). The product was obtained as yellow needles in 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.46 (s, 1H, N=CH), 8.40 (d, 1H, quin), 8.27 (d, 1H, quin), 8.17 (br, 1H, OH), 7.48 (t, 1H, quin), 7.41 (d, 1H, quin), 7.23 (d, 1H, quin), 7.11−7.07 (m, 4H, Ar H), 7.04 (d, 1H, Ar H).

$[ONN^{Me}]H_2$ (Lb). Using the same procedure as for the synthesis of **La**, **Lb** was obtained as yellow crystals by the reaction of 8-hydroxy-2-quinolinecarbaldehyde (0.6 g, 3.5 mmol) and 2,6-dimethylphenylamine (0.42 g, 3.5 mmol) in a yield of 78%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.48 (s, 1H, N=CH), 8.42 (d, 1H, quin), 8.28 (d, 1H, quin), 8.18 (br, 1H, OH), 7.56 (t, 1H, quin), 7.41 (d, 1H, quin), 7.23 (d, 1H, quin), 7.11 (d, 2H, Ar H), 7.02 (d, 1H, Ar H), 2.22 (s, 6H, $2CH_3$).

$[ONN^{Et}]H_2$ (Lc). Using the same procedure as for the synthesis of **La**, **Lc** was obtained as yellow crystals by the reaction of 8-hydroxy-2-quinolinecarbaldehyde (0.6 g, 3.5 mmol) and 2,6-diethylphenylamine (0.52 g, 3.5 mmol) in a yield of 76%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.47 (s, 1H, N=CH), 8.44 (d, 1H, quin), 8.27 (d, 1H, quin), 8.14 (br, 1H, OH), 7.59 (t, 1H, quin), 7.48 (d, 1H, quin), 7.33 (d, 1H, quin), 7.21 (d, 2H, Ar H), 7.08 (d, 1H, Ar H), 2.58 (m, 4H, $2CH_2$), 1.27 (t, 6H, $2CH_3$).

$[ONN^{iPr}]H_2$ (Ld). Using the same procedure as for the synthesis of **La**, **Ld** was obtained as yellow crystals by the reaction of 8-hydroxy-2-quinolinecarbaldehyde (0.6 g, 3.5 mmol) and 2,6-diisopropylphenylamine (0.62 g, 3.5 mmol) in a yield of 72%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.47 (d, 1H, quin), 8.40 (d, 1H, quin), 8.37 (s, 1H, N=CH), 8.22 (br, 1H, OH), 7.77 (t, 1H, quin), 7.45 (d, 1H, quin), 7.23 (d, 1H, quin), 7.16 (d, 2H, Ar H), 7.08 (d, 1H, Ar H), 3.49 (sept, 2H, CH ^{i}Pr), 1.21 (d, 6H, $2CH_3$), 1.15 (d, 6H, $2CH_3$).

$[ONN^{Cl}]H_2$ (Le). 8-Hydroxy-2-quinolinecarbaldehyde (0.6 g, 3.5 mmol) and 2,6-dichlorophenylamine (0.56 g, 3.5 mmol) were dissolved in 40 mL of dry methanol in a 100 mL round-bottom flask. Four drops of methanoic acid were added. The reaction mixture was refluxed for 10 h and cooled to room temperature. Purification by column chromatography used 1/10 ethyl acetate/petroleum ether. The product was obtained as yellow needles in 25% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.63 (s, 1H, N=CH), 8.44 (d, 1H, quin), 8.30 (d, 1H, quin), 8.17 (br, 1H, OH), 7.55 (t, 1H, quin), 7.41 (t, 3H, Ar H), 7.25 (d, 1H, quin), 7.06 (d, 1H, quin).

$CpZr[ONN^H]Cl_2$ (1a). To a stirred suspension of NaH (48 mg, 2.0 mmol) in 10 mL of THF was added **La** (62 mg, 0.25 mmol) dropwise at 0 °C. Stirring was maintained for 2 h at room temperature. The mixture was filtered. The filtrate was cooled to −78 °C and added dropwise to a solution of $CpZrCl_3$ (66 mg, 0.25 mmol) in 15 mL of THF. The resulting suspension was warmed to room temperature and stirred overnight, and the solvent was removed under vacuum. The residue was extracted with 20 mL of toluene to remove NaCl salt. Removal of volatiles under vacuum left a red powder. Recrystallization of the product from toluene/pentane afforded **1a** as a dark red powder in a yield of 73%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.52 (s, 1H, N=CH), 8.46 (d, 1H, quin), 7.80 (d, 1H, quin), 7.74 (t, 1H, quin), 7.41 (d, 1H, quin), 7.29 (d, 1H, quin), 7.25−7.18 (m, 4H, Ar H), 7.13 (d, 1H, Ar H), 6.55 (s, 5H, Cp H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.24, 165.1, 148.3, 144.29, 142.0, 139.8, 132.7, 130.2, 128.7, 127.4, 126.0, 121.2, 118.7, 116.8, 116.0 ppm. Anal. Calcd for $C_{21}H_{16}Cl_2N_2OZr$: C, 53.16; H, 3.40; N, 5.90. Found: C, 53.44; H, 3.90; N, 5.69.

$CpZr[ONN^{Me}]Cl_2$ (1b). This complex was prepared as described above for **1a,** starting from NaH (48 mg, 2.0 mmol), **Lb** (70 mg, 0.25 mmol), and $CpZrCl_3$(66 mg, 0.25 mmol). Workup afforded **1b** as orange crystals in a yield of 78%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.53 (s, 1H, N=CH), 8.52 (d, 1H, quin), 7.87 (d, 1H, quin), 7.77 (t, 1H, quin), 7.44 (d, 1H, quin), 7.23−7.15 (m, 3H, Ar H), 7.13 (d, 1H, quin), 6.55 (s, 5H, Cp H), 2.47 (s, 6H, $2CH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.4, 164.5, 149.44, 142.3, 139.1, 134.0, 130.9, 129.8, 129.0, 128.2, 127.5, 125.3, 122.0, 118.9, 115.4, 20.1 ppm. Anal. Calcd for $C_{23}H_{20}Cl_2N_2OZr$: C, 54.97; H, 4.01; N, 5.57. Found: C, 54.83; H, 4.27; N, 5.18.

$CpZr[ONN^{Et}]Cl_2$ (1c). This complex was prepared as described above for **1a,** starting from NaH (48 mg, 2.0 mmol), **Lc** (76 mg, 0.25 mmol), and $CpZrCl_3$ (66 mg, 0.25 mmol). Workup afforded **1c** as orange-red crystals in a yield of 75%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.56 (s, 1H, N=CH), 8.50 (d, 1H, quin), 7.84 (d, 1H, quin), 7.67 (t, 1H, quin), 7.46 (d, 1H, quin), 7.24−7.17 (m, 3H, Ar H), 7.05 (d, 1H, quin), 6.54 (s, 5H, Cp H), 3.25−3.17 (m, 1H, CH_2), 3.14−3.10 (m, 1H, CH_2), 3.05−3.00 (m, 1H, CH_2), 2.89−2.85 (m, 1H, CH_2), 1.59 (t, 3H, CH_3), 1.12 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.9, 166.0, 148.5, 143.1, 141.7, 138.7, 134.7, 131.9, 129.2, 128.6, 127.6, 125.2, 122.3, 116.7, 115.1, 24.9, 14.7 ppm. Anal. Calcd for $C_{25}H_{24}Cl_2N_2OZr$: C, 56.59; H, 4.56; N, 5.28. Found: C, 56.63; H, 4.62; N, 5.19.

$CpZr[ONN^{iPr}]Cl_2$ (1d). This complex was prepared as described above for **1a,** starting from NaH (48 mg, 2.0 mmol), **Ld** (83 mg, 0.25 mmol), and $CpZrCl_3$(66 mg, 0.25 mmol). Workup afforded **1d** as orange crystals in a yield of 81%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.53 (s, 1H, N=CH), 8.43 (d, 1H, quin), 7.87 (d, 1H, quin), 7.78 (t, 1H, quin), 7.36−7.26 (m, 2H, quin), 7.25−7.15 (m, 3H, Ar H), 6.55 (s, 5H, Cp H), 3.64 (sept, 2H, CH^{i}Pr), 1.41 (d, 6H, $2CH_3$), 1.04 (d, 6H, $2CH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.54, 164.6, 147.3, 142.2, 140.8, 139.1, 137.9, 134.1, 129.0, 128.4, 125.3, 124.6, 121.9, 118.9, 115.6, 27.9, 25.9, 23.2 ppm. Anal. Calcd for $C_{27}H_{28}Cl_2N_2OZr$: C, 58.05; H, 5.05; N, 5.01. Found: C, 58.05; H, 5.15; N, 4.87.

CpZr[ONN^{Cl}]Cl$_2$ (1e). This complex was prepared as described above for **1a,** starting from NaH (48 mg, 2.0 mmol), **Le** (79 mg, 0.25 mmol), and $CpZrCl_3$(66 mg, 0.25 mmol). Workup afforded **1e** as a brown powder in a yield of 61%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.68 (s, 1H, N=CH), 8.57 (d, 1H, quin), 8.41 (d, 1H, quin), 7.61 (t, 1H, quin), 7.56 (t, 3H, Ar H), 7.25 (d, 1H, quin), 7.06 (d, 1H, quin), 6.55 (s, 5H, Cp H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.9, 166.2, 151.0, 146.3, 144.7, 139.1, 135.4, 134.2, 130.7, 129.9, 127.5, 124.8, 121.5, 119.2, 118.5 ppm. Anal. Calcd for $C_{21}H_{14}Cl_4N_2OZr$: C, 46.42; H, 2.60; N, 5.16. Found: C, 46.49; H, 2.49; N, 5.35.

Cp*Zr[ONN^{H}]Cl$_2$ (2a). This complex was prepared as described above for **1a,** starting from NaH (48 mg, 2.0 mmol), **La** (62 mg, 0.25 mmol), and Cp^*ZrCl_3 (82.6 mg, 0.25 mmol). Workup afforded **2a** as orange crystals in a yield of 75%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.50 (s, 1H, N=CH), 8.45 (d, 1H, quin), 7.78 (d, 1H, quin), 7.74 (t, 1H, quin), 7.40 (d, 1H, quin), 7.29 (d, 1H, quin), 7.25−7.18 (m, 4H, Ar H), 7.11 (d, 1H, Ar H), 1.92 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.3, 165.2, 148.4, 144.2, 141.9, 140.0, 133.0, 129.9, 128.7, 127.8, 125.9, 121.4, 118.6, 116.7, 116.2, 11.9 ppm. Anal. Calcd for $C_{26}H_{26}Cl_2N_2OZr$: C, 57.34; H, 4.81; N, 5.14. Found: C, 57.37; H, 4.79; N, 5.17.

Cp*Zr[ONN^{Me}]Cl$_2$ (2b). This complex was prepared as described above for **1a,** starting from NaH (48 mg, 2.0 mmol), **Lb** (70 mg, 0.25 mmol), and Cp^*ZrCl_3 (82.6 mg, 0.25 mmol). Workup afforded **2b** as orange crystals in a yield of 70%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.56 (s, 1H, N=CH), 8.43 (d, 1H, quin), 7.77 (d, 1H, quin), 7.69 (t, 1H, quin), 7.32 (d, 1H, quin), 7.25 (d, 1H, quin), 7.25−7.13 (m, 2H, Ar H), 7.01 (d, 1H, Ar H), 2.36 (s, 6H, $2CH_3$), 1.92 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.9, 164.7, 148.4, 142.2, 138.3, 133.5, 130.6, 129.0, 128.2, 126.9, 126.5, 126.1, 125.2, 122.3, 114.9, 20.1, 11.5 ppm. Anal. Calcd for $C_{28}H_{30}Cl_2N_2OZr$: C, 58.72; H, 5.28; N, 4.89. Found: C, 58.74; H, 5.30; N, 4.85.

Cp*Zr[ONN^{Et}]Cl$_2$ (2c). This complex was prepared as described above for **1a,** starting from NaH (48 mg, 2.0 mmol), **Lc** (76 mg, 0.25 mmol), and Cp^*ZrCl_3(82.6 mg, 0.25 mmol). Workup afforded **2c** as orange crystals in a yield of 69%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.55 (s, 1H, N=CH), 8.50 (d, 1H, quin), 7.83 (d, 1H, quin), 7.74 (t, 1H, quin), 7.36 (d, 1H, quin), 7.30 (d, 1H, quin), 7.23−7.11 (m, 2H, Ar H), 7.05 (d, 1H, Ar H), 3.24−3.18 (m, 1H, CH_2), 3.12−3.08 (m, 1H, CH_2), 3.00−2.95 (m, 1H, CH_2), 2.87−2.82 (m, 1H, CH_2), 1.50 (t, 3H, CH_3), 1.23 (t, 3H, CH_3), 1.93 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.1, 166.3, 148.7, 143.6, 142.1, 138.7, 135.1, 131.9, 130.2, 128.1, 127.6, 126.0, 123.1, 116.5, 115.4, 24.8, 14.6, 11.7 ppm. Anal. Calcd for $C_{30}H_{34}Cl_2N_2OZr$: C, 59.98; H, 5.70; N, 4.66. Found: C, 59.92; H, 5.74; N, 4.69.

Cp*Zr[ONN^{iPr}]Cl$_2$ (2d). This complex was prepared as described above for **1a,** starting from NaH (48 mg, 2.0 mmol), **Ld** (83 mg, 0.25 mmol), and Cp^*ZrCl_3 (82.6 mg, 0.25 mmol). Workup afforded **2d** as orange crystals in a yield of 68%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.51 (s, 1H, N=CH), 8.43 (d, 1H, quin), 7.75 (d, 1H, quin), 7.68 (t, 1H, quin), 7.32−7.27 (m, 2H, quin), 7.25−7.23 (m, 2H, Ar H), 7.24 (d, 1H, Ar H), 3.58 (sept, 2H, $2CH(^iPr)$), 1.92 (s, 15H, $C_5(CH_3)_5$), 1.33 (d, 6H, $2CH_3$), 0.97 (d, 6H, $2CH_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.5, 164.8, 146.8, 142.0, 141.0, 138.4, 133.5, 130.7, 129.0, 128.2, 126.2, 123.9, 122.2, 114.9, 114.4, 27.4, 26.0, 22.7, 11.8 ppm. Anal. Calcd for $C_{32}H_{38}Cl_2N_2OZr$: C, 61.12; H, 6.09; N, 4.46. Found: C, 61.18; H, 6.11; N, 4.51.

Cp*Zr[ONN^{Cl}]Cl$_2$ (2e). This complex was prepared as described above for **1a,** starting from NaH (48 mg, 2.0 mmol), **Le** (79 mg, 0.25 mmol), and Cp^*ZrCl_3 (82.6 mg, 0.25 mmol). Workup afforded **2e** as a brown powder in a yield of 55%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.73 (s, 1H, N=CH), 8.61 (d, 1H, quin), 8.45 (d, 1H, quin), 7.89 (t, 1H, quin), 7.65 (m, 3H, Ar H), 7.25 (d, 1H, quin), 7.06 (d, 1H, quin), 1.92 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.8, 166.6, 152.1, 147.0, 145.1, 138.9, 135.2, 134.8, 130.9, 129.9, 127.1, 124.6, 122.0, 119.7, 118.0, 11.9 ppm. Anal. Calcd for $C_{26}H_{24}Cl_4N_2OZr$: C, 50.90; H, 3.94; N, 4.57. Found: C, 51.32; H, 3.71; N, 4.80.

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Supporting Information Available: CIF files, tables and figures giving crystallographic data, details of the refinement, and ORTEP diagrams of complexes **1b**,**d** and **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.