Synthesis, characterization, and catalytic properties of new half-sandwich zirconium(IV) complexes

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A number of new half-sandwich zirconium(IV) complexes bearing N,N-dimethylalaniline-amido ligands with the general formula Cp*ZrCl2[ortho-(RNCH2)(Me2N)C6H4] [R = 2,6-Me2C6H3 (1), 2,6-iPr2C6H3 (2), iPr (3), Bu (4)] were synthesized by the reaction of Cp*ZrCl3 with the corresponding ortho-(Me2N)C6H4CH2NRLi. All new zirconium complexes were characterized by 1H and 13C NMR, elemental analyses and single-crystal X-ray diffraction analysis. The molecular structural analysis reveals that the NMe2 group does not coordinate to the zirconium atom in all cases. Complexes 1–4 all have a pseudo-tetrahedral coordination environment in their solid state structures and adopt a three-legged piano stool geometry for the zirconium atoms with the amide N atom and the two Cl atoms being the three legs and the Cp* ring being the seat. Variable-temperature 1H NMR experiments for all complexes 1–4 were performed to investigate the possible intramolecular interaction between the N atom in the NMe2 group and the central zirconium atom in solution. Upon activation with AlBu3 and Ph3CB(C6F5)4, complexes 1–4 all exhibit moderate to good catalytic activity for ethylene polymerization and copolymerization with 1-hexene, producing linear polyethylene or poly(ethylene-co-1-hexene) with moderate molecular weight and reasonable 1-hexene incorporation.

Introduction

Group 4 metallocene catalysts have attracted extensive interest in academic and industrial institutes due to their unique properties and advantages as olefin polymerization catalysts. Many research efforts have been focused on the development of new homogeneous metallocene catalysts for producing high performance polyolefin materials with tailored structures and properties.1–6 Zirconocene complexes have been widely explored as efficient catalysts for ethylene6 and propylene4,8 polymerization and copolymerization with higher Ω-olefins.9 Some nonbridged and bridged zirconocene complexes have been found to exhibit unique catalytic characteristics for stereospecific polymerization of propylene.10–14 Since constrained geometry and nonbridged monocyclopentadienyl titanium complexes have been known to be good catalysts for ethylene copolymerization with Ω-olefins,15 some nonbridged monocyclopentadienyl zirconium complexes bearing a benzamidinate,16 aryloxide,17 salicyaldiminato,18 β-diketiminate19 or imino-quinolinol20 ligand were also synthesized and tested as catalysts for ethylene polymerization and copolymerization with Ω-olefins. In addition, some non-metallocene types of zirconium complexes were also synthesized and studied as catalysts for olefin polymerization.21,22 Recently, we reported a number of monocyclopentadienyl zirconium anilide complexes Cp*ZrCl2[N(2,6-RiC6H4)C6H2(CH2NRLi) which exhibit moderate catalytic activity for ethylene copolymerization with 1-hexene and produce copolymers with relatively high molecular weight and reasonable 1-hexene incorporation.23 To further modify the structure of the half-sandwich zirconium complexes, we have synthesized a number of new monocyclopentadienyl zirconium(IV) complexes bearing a N,N-dimethylalaniline-amido ligand with the general formula Cp*ZrCl2[ortho-(RNCH2)(Me2N)C6H4] [R = 2,6-Me2C6H3 (1), 2,6-iPr2C6H3 (2), iPr (3), Bu (4)], and investigated their catalytic properties for ethylene polymerization. Herein we report the synthesis, characterization and crystal structure of these half-sandwich zirconium complexes, as well as their catalytic performance for ethylene polymerization and copolymerization with 1-hexene.

Results and discussion

Synthesis and characterization of new compounds

The free ligands ortho-(Me2N)C6H4CH2NHR [R = 2,6-Me2C6H3 (HLa), 2,6-iPr2C6H3 (HLe), iPr (HLc), Bu (HLd)] were synthesized according to a literature procedure.24 The new zirconium(IV) complexes 1–4 were synthesized in Et2O by the reaction of Cp*ZrCl3 with ortho-(Me2N)C6H4CH2NRLi which were prepared in situ by treating the corresponding ortho-
The synthetic procedure of complexes 1–4.

\[
\begin{align*}
R &= \text{2.5-Me}_2\text{C}_6\text{H}_5 (\text{La}) \\
R &= \text{2.5-Pr}_2\text{C}_6\text{H}_3 (\text{Lb}) \\
R &= \text{Pr} (\text{Lc}) \\
R &= \text{Bu} (\text{Ld}) \\
\end{align*}
\]

Scheme 1

\[
\begin{align*}
\text{Me}_2\text{N} &\equiv \text{C}_6\text{H}_4\text{CH}_2\text{NHR} \\
\end{align*}
\]

(Me₂N)C₆H₄CH₂NHR with 1 equiv of nBuLi in n-hexane as shown in Scheme 1. Analytical pure samples were obtained as orange or pale-yellow crystalline solids in moderate yields (65–80%) from a concentrated dichloromethane solution layered with n-hexane at −30 °C. These new zirconium complexes 1–4 were all characterized by ¹H and ¹³C NMR spectroscopy, elemental analyses, and single-crystal X-ray diffraction analysis.

The ¹H NMR spectra of complexes 1–4 show that the resonances of the N–CH₂ protons appear at 5.20, 4.97, 4.67, and 4.23 ppm, respectively, which are obviously shifted down-field in comparison to the corresponding signals in the free ligands (4.17, 4.07, 3.85 and 3.79 ppm, respectively). The resonance of the N–CHMe₂ proton (4.60 ppm) in complex 3 is also shifted toward down-field compared with the corresponding signal in the free ligand HLa (2.77 ppm). On the other hand, the resonances for the methyl protons in the N-2,6-Me₂C₆H₃ group in complex 1 (1.77 ppm) and the methine protons in the N-2,6-Pr₂C₆H₃ group in complex 2 (3.26 ppm) are shifted to up-field from those in the corresponding free ligands (2.30 and 3.41 ppm for HLa and HLb, respectively). The above observations are indicative of the formation of the Zr–N (amide) bond in these complexes. The resonances of the NMe₂ protons in complexes 1 (2.03 ppm) and 2 (2.16 ppm) are obviously shifted up-field from those in the corresponding free ligands (2.72 and 2.73 ppm for HLa and HLB, respectively), while the resonances for the NMe₂ protons in complexes 3 (2.69 ppm) and 4 (2.71 ppm) are almost the same as those in the free ligands HLe (2.70 ppm) and HLD (2.71 ppm). The single crystal X-ray diffraction analysis indicates that the NMe₂ group does not coordinate to the central zirconium atom in these complexes in the solid state. For complex 2, the four methyl groups in the two Pr substituents give two sets of doublets (0.71 and 1.23 ppm) in its ¹H NMR spectrum and correspondingly two signals (24.8 and 25.6 ppm) in its ¹³C NMR spectrum due to the restricted rotation of the 2,6-Pr₂C₆H₃ group about the N–C bond.¹⁵p,²³,²⁵

It was noticed that the N–CH₂ protons in complex 4 show a broad signal around 4.23 ppm at room temperature (293 K). Variable-temperature ¹H NMR experiments indicate that the resonance gets sharp at 313 K, but splits into two signals with decreasing the temperature and becomes a pair of doublets (3.42 and 4.89 ppm, ²J_H,H = 16 Hz) at 233 K as shown in Fig. 1. These phenomena may result from possible coordination of the NMe₂ group to the central Zr atom (process A) or restricted rotation of the amido group about the Zr–N bond (process B) at low temperature as illustrated in Scheme 2. If the NMe₂ group can coordinate to the central Zr atom at low temperatures, similar results should be observed for complexes 1, 2 and 3. However, no obvious change for the signals of the N–CH₂ protons was observed for complexes 1–3 in similar variable-temperature ¹H NMR experiments. In addition, the resonance of the NMe₂ protons shows little change with changing the temperature, which is in contrast to the proposed process A. It is obvious that the observed phenomena with complex 4 are more likely caused by process B since the bulky Bu group on the amido N atom in complex 4 would slow down the rotation rate of the amido group about the Zr–N bond.

Crystal structures of complexes 1–4

Molecular structures of complexes 1–4 were determined by single crystal X-ray diffraction analysis. The ORTEP drawings of their molecular structures together with data of selected bond lengths and angles are given in Figs 2–5, respectively. Detailed crystallography information can be found in the supplementary information.† Crystallographic data indicate that complexes 1–3 crystallize in a monoclinic system with space group P2₁/C while complex 4 crystallizes in a triclinic system with space group P1.

Complexes 1–4 all have a pseudo-tetrahedral coordination environment around their metal centers in the solid state.
structures and adopt a three-legged piano stool geometry with the N(1) atom and the two Cl atoms being the three legs and the Cp* ring being the seat. As seen in previously reported complexes \( \text{Cp}^+\text{MCl}_2[\text{N}(2,6-\text{R}_3\text{C}_6\text{H}_3)](\text{CH}_3) \) (\( \text{M} = \text{Ti, Zr; } \text{R} = \text{Me, } ^\text{Pr} \)), the aryl ring directly bonded to the N(1) atom in complex 1 is nearly parallel to the Cp* ring with an angle of 11.5°. The Zr–N(1) distance in complex 2 (2.040 Å) is slightly longer than those in complexes 1 (2.0177 Å), 3 (2.007 Å) and 4 (2.0218 Å). The average Zr–Cl distances in complexes 1 (2.4152 Å), 2 (2.3985 Å), 3 (2.4206 Å) and 4 (2.4206 Å) are close to those reported in complexes \( \text{Cp}^+\text{ZrCl}_2[\text{N}(2,6-\text{R}_3\text{C}_6\text{H}_3)](\text{CH}_3) \) (\( \text{R} = ^\text{Pr}, 2.414 \text{ Å}; \text{R} = \text{Me, } 2.403 \text{ Å} \)). The \( \text{Cp}^+\text{(cent)}–\text{Zr}–\text{Cl} \) distances in complexes 1 (2.022 Å), 2 (2.220 Å), 3 (2.198 Å) and 4 (2.216 Å) are close to those reported in complexes \( \text{Cp}^+\text{ZrCl}_2[\text{N}(2,6-\text{R}_3\text{C}_6\text{H}_3)](\text{CH}_3) \) (\( \text{R} = ^\text{Pr}, 2.197 \text{ Å}; \text{R} = \text{Me, } 2.214 \text{ Å} \)). The Cl(1)–Zr(1)–Cl(2) angles in these complexes decrease in the order of 1 (107.1°) > 2 (103.3°) > 3 (104.8°) > 4 (100.18°) with the change in the steric bulk of the N–R group. The sum of the bond angles around the N atom is close to 360° for all complexes, indicating the N atom forming bonds with sp² orbitals in these complexes. The \( \text{Cp}^+\text{(cent)}–\text{Zr}(1)–\text{N}(1) \) angles in complex 1 (122.1°) are larger than those in complexes 2 (121.1°) and 3 (116.6°) and 3 (115.4°), which is obviously caused by the bulky N–R group in the former complexes.

**Fig. 2** A perspective view of 1 with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (°): \( \text{Cp}^+\text{(cent)}–\text{Zr}(1) = 2.202, \text{Zr}(1)–\text{N}(1) = 2.040(9), \text{Zr}(1)–\text{Cl}(1) = 2.387(4), \text{Zr}(1)–\text{Cl}(2) = 2.410(4), \text{Cl}(1)–\text{Zr}(1)–\text{Cl}(2) = 105.30(17), \text{N}(1)–\text{Zr}(1)–\text{Cl}(1) = 103.9(3), \text{N}(1)–\text{Zr}(1)–\text{Cl}(2) = 103.0(3), \text{C}(11)–\text{N}(1)–\text{Zr}(1) = 124.9(7), \text{C}(23)–\text{N}(1)–\text{Zr}(1) = 121.1(7), \text{C}(11)–\text{N}(1)–\text{C}(23) = 113.7(8), \text{Cp}^+\text{(cent)}–\text{Zr}(1)–\text{Cl}(1) = 109.9, \text{Cp}^+\text{(cent)}–\text{Zr}(1)–\text{Cl}(2) = 109.2, \text{Cp}^+\text{(cent)}–\text{Zr}(1)–\text{N}(1) = 123.9.\)

**Fig. 3** A perspective view of 2 with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (°): \( \text{Cp}^+\text{(cent)}–\text{Zr}(1) = 2.220, \text{Zr}(1)–\text{N}(1) = 2.040(9), \text{Zr}(1)–\text{Cl}(1) = 2.413(4), \text{Zr}(1)–\text{Cl}(2) = 2.419(4), \text{Cl}(1)–\text{Zr}(1)–\text{Cl}(2) = 105.30(17), \text{N}(1)–\text{Zr}(1)–\text{Cl}(1) = 103.9(3), \text{N}(1)–\text{Zr}(1)–\text{Cl}(2) = 103.0(3), \text{C}(11)–\text{N}(1)–\text{Zr}(1) = 124.9(7), \text{C}(23)–\text{N}(1)–\text{Zr}(1) = 121.1(7), \text{C}(11)–\text{N}(1)–\text{C}(23) = 113.7(8), \text{Cp}^+\text{(cent)}–\text{Zr}(1)–\text{Cl}(1) = 109.9, \text{Cp}^+\text{(cent)}–\text{Zr}(1)–\text{Cl}(2) = 109.2, \text{Cp}^+\text{(cent)}–\text{Zr}(1)–\text{N}(1) = 123.9.\)

**Fig. 4** A perspective view of 3 with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (°): \( \text{Cp}^+\text{(cent)}–\text{Zr}(1) = 2.198, \text{Zr}(1)–\text{N}(1) = 2.007(2), \text{Zr}(1)–\text{Cl}(1) = 2.4221(7), \text{Zr}(1)–\text{Cl}(2) = 2.4198(7), \text{Cl}(1)–\text{Zr}(1)–\text{Cl}(2) = 104.80(3), \text{N}(1)–\text{Zr}(1)–\text{Cl}(1) = 109.05(6), \text{N}(1)–\text{Zr}(1)–\text{Cl}(2) = 103.25(6), \text{C}(11)–\text{N}(1)–\text{Zr}(1) = 144.40(17), \text{C}(20)–\text{N}(1)–\text{Zr}(1) = 100.35(15), \text{C}(11)–\text{N}(1)–\text{C}(20) = 115.2(2), \text{Cp}^+\text{(cent)}–\text{Zr}(1)–\text{Cl}(1) = 110.9, \text{Cp}^+\text{(cent)}–\text{Zr}(1)–\text{Cl}(2) = 112.7, \text{Cp}^+\text{(cent)}–\text{Zr}(1)–\text{N}(1) = 115.4.\)

**Fig. 5** A perspective view of 4 with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (°): \( \text{Cp}^+\text{(cent)}–\text{Zr}(1) = 2.216, \text{Zr}(1)–\text{N}(1) = 2.0218(16), \text{Zr}(1)–\text{Cl}(1) = 2.4190(5), \text{Zr}(1)–\text{Cl}(2) = 2.4231(5), \text{Cl}(1)–\text{Zr}(1)–\text{Cl}(2) = 100.18(2), \text{N}(1)–\text{Zr}(1)–\text{Cl}(1) = 102.42(5), \text{N}(1)–\text{Zr}(1)–\text{Cl}(2) = 107.45(5), \text{C}(11)–\text{N}(1)–\text{Zr}(1) = 143.53(15), \text{C}(19)–\text{N}(1)–\text{Zr}(1) = 106.13(13), \text{C}(11)–\text{N}(1)–\text{C}(19) = 113.87(17), \text{Cp}^+\text{(cent)}–\text{Zr}(1)–\text{Cl}(1) = 110.8, \text{Cp}^+\text{(cent)}–\text{Zr}(1)–\text{Cl}(2) = 111.2, \text{Cp}^+\text{(cent)}–\text{Zr}(1)–\text{N}(1) = 116.6.\)
Polymerization reaction

Ethylene polymerization using complexes 1–4 as precatalysts under different conditions was studied in detail and the results are summarized in Table 1. Upon activation with Al(i-Pr)3 and Ph3CB(C6F5)4, complexes 1–4 all exhibit good catalytic activity for ethylene polymerization. Under similar conditions, the catalytic activity decreases in the order of 4 > 3 > 1 > 2, indicating that the catalytic activity of these zirconium complexes is remarkably influenced by the nature of the substituents on the amido ligands. As observed in other zirconocene catalyst systems, the catalytic activity of these zirconium catalyst systems is dependent on the Al/Zr molar ratio. The maximal catalytic activities were obtained at Al/Zr molar ratios of about 350. The catalytic activity of these catalyst systems is evidently dependent on the structure of the catalyst. The comonomer content of the copolymers obtained with complexes 1, 2 and 4 is obviously higher than that of the copolymer produced by complex 3 under similar conditions. It has been known that the comonomer incorporation ability of a catalyst system can be affected by several factors. In the present work, the steric bulk of the amido ligand seems to be a major issue. A large steric hindrance from the ligands would weaken the interaction between the cationic catalyst and the anionic cocatalyst species, which would favor the coordination of the comonomer to the metal center of the catalyst.GPC analysis on the copolymers reveals that the poly(ethylene-co-1-hexene)s produced by these catalysts possess moderate molecular weight (Mn = 6.8–12.0 × 10^4 g mol⁻¹). The molecular weight distribution is basically unimodal and narrow, being characteristic for metallocene polyolefins. In addition, the melting temperatures of the resultant copolymers are in the range of 127–130 °C.

Conclusions

A number of new half-sandwich zirconium (iv) complexes 1–4 of the type Cp*ZrCl2[ortho-(RNCH2)(Me2N)C6H4] were synthesized by the reaction of Cp*ZrCl3 with ortho-C6H4(NMe2)CH2NRLi in moderate yields. All new complexes were characterized by 1H and 13C NMR, elemental analyses, and single crystal X-ray diffraction analysis.

Table 1 A summary of ethylene polymerization catalyzed by 1–4/Al(i-Pr)3/Ph3CB(C6F5)4 systems

<table>
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<th>Run</th>
<th>Catalyst</th>
<th>T°C</th>
<th>Al/Zr molar ratio</th>
<th>Yield (g)</th>
<th>Activityb</th>
<th>Mw × 10⁻⁴</th>
<th>Mn/Mw</th>
<th>Tm,c (°C)</th>
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<td>1760</td>
<td>3.60</td>
<td>2.22</td>
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</table>

a Polymerization conditions: toluene 70 mL, catalyst 2 μmol Zr, B/Zr molar ratio 1.5, time 15 min, ethylene pressure 5 bar. b Activity in g PE (mmol Zr)⁻¹ h⁻¹. c Determined by GPC in o-dicholobenzene vs. polystyrene standard.

Table 2 A summary of ethylene/1-hexene copolymerization catalyzed by 1–4/Al(i-Pr)3/Ph3CB(C6F5)4 systems

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>Yield (g)</th>
<th>Activityb</th>
<th>1-hexene content (mol%)</th>
<th>Mw,d × 10⁻⁴</th>
<th>Mn/Mw</th>
<th>Tm,c (°C)</th>
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<td>3.76</td>
<td>5.81</td>
<td>3.12</td>
<td>127.2</td>
</tr>
</tbody>
</table>

a Polymerization conditions: toluene + 1-hexene total 70 mL, catalyst 2 μmol Zr, Al/Zr molar ratio 350, B/Zr molar ratio 1.5, time 15 min, temperature 80 °C, ethylene pressure 5 bar. b Activity in g polymer (mmol Zr)⁻¹ h⁻¹. c Determined by DSC at a heating rate of 10 °C min⁻¹ and the data from the second scan are used.
crystal X-ray diffraction analysis. The molecular structural analysis reveals that the NM2 group does not coordinate to the zirconium atom in all cases. Complexes 1–4 all have a pseudo-tetrahedral coordination environment in their solid state structures and adopt a three-legged piano stool geometry for the zirconium atoms with the amide N atom and the two Cl atoms being the three legs and the Cp ring being the seat. Upon activation with AlBu3/Ph3CB(C6F5)2, complexes 1–4 all exhibit good catalytic activity for ethylene polymerization and ethylene/1-hexene copolymerization, producing moderate molecular weight polyethylenes and relatively high molecular weight poly(ethylene-co-1-hexene) with reasonable 1-hexene incorporation.

**Experimental section**

**General comments**

All manipulations involving air and moisture sensitive compounds were carried out under nitrogen atmosphere (ultra-high purity) using either standard Schlenk techniques or glove box techniques. Toluene, diethyl ether, THF, and n-hexane were distilled under nitrogen in the presence of sodium and benzophenone. CH2Cl2 and 1-hexene were purified by distilling over calcium hydride before use. Cp∗ZrCl3,28 HLa, HLB, ortho-C8H4(NMe)2CHO24 and Ph3CB(C6F5)329 were prepared according to literature procedures. Polymerization grade ethylene was further purified by passage through columns of 5 Å molecular sieves and MnO. AlBu3,4 BuLi, and ZrCl4 were purchased from Aldrich or Acros.11 H and 13C NMR spectra were measured using a Varian Mercury-300 NMR spectrometer.13C NMR spectra of the copolymers were recorded on a Varian Unity-400 NMR spectrometer at 125 °C with o-C6D4Cl2 as the solvent. Molecular weight and molecular weight distribution of the polymer samples were measured on a PL-GPC 220 at 140 °C with 1,2,4-trichlorobenzene as the solvent. The melting points of the polymers were measured by differential scanning calorimetry (DSC) on a NETZSCH DSC 204 at a heating/cooling rate of 10 °C min−1 from 35 to 180 °C and the data from the second heating scan were used.

**Synthesis of ortho-C6H4NMe2CH2NHPr (HLc).** ortho-C6H4(NMe)2CHO (2.24 g, 15.0 mmol) and PrNH2 (0.887 g, 15.0 mmol) were dissolved in 20 mL of methanol. To the mixture was added a catalytic amount of formic acid. The reaction mixture was allowed to warm to room temperature and stirred over night. The reaction mixture was added a catalytic amount of formic acid. The reaction mixture was allowed to warm to room temperature and stirred over night. The resultant precipitate was filtered off. Further 40 mL of H2O was added to the filtrate and the product was extracted with 50 mL of diethyl ether. The organic phase was separated, dried over anhydrous MgSO4, filtered off. Further 40 mL of H2O was added to the filtrate and the product was extracted with 50 mL of diethyl ether. The final product HLa (2.50 g, 12.1 mmol, 93%) was obtained as an orange oil.

**Synthesis of ortho-C6H4NMe2CH2NHBu (HLd).** HLd was synthesized using a procedure identical to that for HLa with ortho-C6H4(NMe)2CHO (2.12 g, 14.2 mmol) and BuNH2 (1.04 g, 14.2 mmol) as the starting materials. The Schiff base product ortho-C6H4NMe2CH=NBu (2.67 g, 13.1 mmol) was obtained in a yield of 92%.1H NMR (CDCl3, 300 MHz, 298 K): δ 8.59 (s, 1 H, CH = N), 7.82 (d, 1 H, ArH, JHH = 7.8 Hz), 7.32 (t, 1 H, ArH, JHH = 7.8 Hz), 6.05–7.08 (m, 2 H, ArH), 2.76 (s, 6 H, N(CH3)2), 1.32 (s, 9 H, Bu) ppm. The final product HLd (2.50 g, 12.1 mmol, 93%) was obtained as an orange oil.

**Synthesis of ortho-C6H4NMe2CH2NH-PrBu (HLc) and ortho-C6H4NMe2CH2NH-PrBu (HLd).** A solution of n-BuLi (4.8 mL, 1.6 M in n-hexane, 7.7 mmol) was added slowly to solution of (ortho-C6H4NMe2CH2)(2,6-Me2C6H3)NH (1.92 g, 7.55 mmol) in hexane at −30 °C, and the reaction mixture was allowed to warm to room temperature and stirred for 15 h. After removal of the solvent, the crude product was extracted with CH2Cl2. Recrystallization from CH2Cl2/n-hexane gave pure complex 1 as orange crystals (0.859 g, 1.57 mmol, 78%). Anal. Calcd. for C27H36Cl2N2Zr (550.70): C, 58.9; H, 6.59; N, 5.09. Found: C, 58.5; H, 6.48; N, 5.06.1H NMR (CDCl3, 300 MHz, 298 K): δ 8.03 (d, 1 H, ArH, JHH = 7.5 Hz), 7.14 (t, 1 H, ArH, JHH = 7.5 Hz), 6.98 (t, 1 H, ArH, JHH = 7.5 Hz), 6.76–6.91 (m, 4 H, ArH), 5.21 (s, 2 H, NCH2), 2.04 (s, 6 H, N(CH3)2), 1.88 (s, 15 H, Cp), 1.78 (s, 6 H, PhMe2) ppm.13C NMR (CDCl3, 75 MHz, 298 K): δ 152.4, 135.6, 130.0, 127.3, 123.3, 119.1, 50.3, 44.9, 43.4, 29.0 ppm.

**Synthesis of complex 1.** LiLa (0.523 g, 2.01 mmol) was added to a suspension of Cp∗ZrCl3 (0.669 g, 2.01 mmol) in 40 mL of diethyl ether at −30 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 h. After removal of the solvent, the crude product was extracted with CH2Cl2. Recrystallization from CH2Cl2/n-hexane gave pure complex 1 as orange crystals (0.859 g, 1.57 mmol, 78%). Anal. Calcd. for C27H36Cl2N2Zr (550.70): C, 58.9; H, 6.59; N, 5.09. Found: C, 58.5; H, 6.48; N, 5.06.1H NMR (CDCl3, 300 MHz, 298 K): δ 8.03 (d, 1 H, ArH, JHH = 7.5 Hz), 7.14 (t, 1 H, ArH, JHH = 7.5 Hz), 6.98 (t, 1 H, ArH, JHH = 7.5 Hz), 6.76–6.91 (m, 4 H, ArH), 5.21 (s, 2 H, NCH2), 2.04 (s, 6 H, N(CH3)2), 1.88 (s, 15 H, Cp), 1.78 (s, 6 H, PhMe2) ppm.13C NMR (CDCl3, 75 MHz, 298 K): δ 154.7, 145.6, 134.5, 133.6, 132.6, 128.6, 127.4, 125.0, 124.6, 124.0, 120.2, 45.3, 44.5, 18.11 ppm.

**Synthesis of complex 2.** Complex 2 was synthesized using a procedure identical to that for complex 1 with LiLb (0.493 g, 1.56 mmol) and Cp∗ZrCl3 (0.519 g, 1.56 mmol) as the starting materials. 0.637 g pure product (1.05 mmol, 67%) was obtained.
### Table 3 Crystallographic parameters, data collections, and structure refinements for complexes 1–4

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<th>4</th>
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<td>C22H34Cl2N2Zr</td>
<td>C23H36Cl2N2Zr</td>
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<td>Triclinic</td>
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<td>P21/c</td>
<td>P21/c</td>
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<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td>β(°)</td>
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<td>20.13(2)</td>
<td>10.2590(6)</td>
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<td>γ(°)</td>
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as orange crystals. Anal. Calcd. for C23H36Cl2N2Zr (606.80): C, 61.4; H, 7.31; N, 4.62. Found: C, 61.1; H, 7.38; N, 4.58. 1H NMR (CDCl3, 300 MHz, 298 K): δ 6.98–7.36 (m, 7 H, ArH), 4.97 (s, 2 H, NCH2), 3.26 (sept, 2 H, CH(CH3)2), 3JH-H = 6.6 Hz), 2.18 (s, 15 H, CpMe3), 2.16 (s, 6 H, Ni(CH3)2), 1.23 (d, 6 H, CH(CH3)2), 3JH-H = 6.6 Hz), 0.71 (d, 6 H, CH(CH3)2), 3JH-H = 6.6 Hz) ppm. 13C NMR (CDCl3, 75 MHz, 298 K): δ 153.9, 146.9, 134.7, 131.5, 128.1, 127.1, 125.4, 124.6, 124.4, 121.5, 53.6, 45.7, 27.9, 25.6, 24.8, 12.2 ppm.

**Synthesis of complex 3.** Complex 3 was synthesized using a procedure identical to that for complex 1 with LiLc (0.369 g, 1.86 mmol) and Cp*ZrCl3 (0.619 g, 1.86 mmol) as the starting materials. 0.635 g pure product (1.30 mol%, 70%) was obtained as orange crystals. Anal. Calcd. for C22H34Cl2N2Zr (488.63): C, 54.1; H, 7.01; N, 5.73. Found: C, 53.7; H, 7.08; N, 5.69. 1H NMR (CDCl3, 300 MHz, 298 K): δ 6.98–7.32 (m, 4 H, ArH), 4.67 (s, 2H, NCH2), 4.60 (sept, 1 H, CH(CH3)2), 3JH-H = 6.0 Hz), 2.69 (s, 6 H, Ni(CH3)2), 2.07 (s, 15 H, CpMe3), 1.07 (d, 6 H, CH (CH3)2), 3JH-H = 6.0 Hz) ppm. 13C NMR (CDCl3, 75 MHz, 298 K): δ 135.9, 146.9, 134.7, 131.5, 128.1, 127.1, 124.3, 123.0, 118.9, 114.6, 46.7, 46.1, 44.9, 22.0, 11.7 ppm.

**Synthesis of complex 4.** Complex 4 was synthesized using a procedure identical to that for complex 1 with LiLd (0.385 g, 1.81 mmol) and Cp*ZrCl3 (0.602 g, 1.81 mmol) as the starting materials. 0.646 g pure product (1.29 mol%, 71%) was obtained as pale yellow crystals. Anal. Calcd. for C23H36Cl2N2Zr (502.66): C, 55.0; H, 7.22; N, 5.57. Found: C, 54.6; H, 7.26; N, 5.59. 1H NMR (CDCl3, 300 MHz, 298 K): δ 7.78 (d, 1 H, ArH), 3JH-H = 7.5 Hz), 7.19 (t, 1 H, ArH), 3JH-H = 7.2 Hz), 7.09 (d, 1 H, ArH, 3JH-H = 7.2 Hz), 7.02(t, 1 H, ArH, 3JH-H = 7.2 Hz), 4.23 (s, 2 H, NCH2), 2.71(s, 6 H, Ni(CH3)2), 2.18 (s, 15 H, CpMe3), 1.05 (s, 9 H, 3Bu) ppm. 13C NMR (CDCl3, 75 MHz, 298 K): δ 152.7, 131.0, 130.8, 127.7, 124.5, 122.5, 118.8, 58.1, 45.2, 35.6, 32.0, 12.2 ppm.

**X-ray structural analysis of complexes 1–4**

Single crystals of complexes 1–4 suitable for X-ray crystal structural analysis were obtained from CH2Cl2/hexane (v/v = 1–2 : 10) mixed solvent system. The data were collected on a Rigaku RAXIS-RAPID diffractometer with Mo-Kα (λ = 0.71073 Å) radiation. All structures were solved by direct method and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions. All calculations were performed using the SHELXTL crystallographic software packages. Details of the crystallographic parameters, data collections, and structure refinements are summarized in Table 3.

**Polymerization reactions**

The ethylene polymerization experiments were carried out as follows: a dry 250 mL steel autoclave with a magnetic stirrer was charged with 60 mL of toluene, thermostatd at a desired temperature and saturated with ethylene (1.0 atm). The polymerization reaction was started by addition of a mixture of catalyst and Al/Al3 in toluene (5 mL) and a solution of Ph3CB(C6F5)4 in toluene (5 mL) at the same time. The vessel was pressurized to 5 atm with ethylene immediately and the pressure was kept by continuous feeding of ethylene. The reaction mixture was stirred at the desired temperature for 15 min. The polymerization was then quenched by injecting acidified methanol [HCl (3 M)/methanol = 1 : 1], and the polymer was collected by filtration, washed with water, methanol, and dried at 60 °C in vacuo to a constant weight. For the ethylene/1-hexene copolymerization experiments, appropriate amounts of 1-hexene were added in toluene.
Acknowledgements

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Notes and references