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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*-dimethylaniline-amido ligands with the general formula Cp*ZrCl₂[*ortho*-(RNCH₂)(Me₂N)C₆H₄] [R = 2,6-Me₂C₆H₃ (1), 2,6-^{*i*}Pr₂C₆H₃ (2), ^{*i*}Pr (3), ^{*i*}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 Al^{*i*}Bu₃ 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 ethylene⁷ and propylene^{4,8} polymerization and copolymerization with higher α -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 α -olefins,¹⁵ some nonbridged monocyclopentadienyl zirconium complexes bearing a benzamidinate,¹⁶ aryloxy,¹⁷ salicylaldiminato,¹⁸ β-diketiminate¹⁹ or imino-quinolinol²⁰ ligand were also synthesized and tested as catalysts for ethylene polymerization and

copolymerization with α -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 $Cp*ZrCl_2[N(2,6-R^1_2C_6H_3)R^2]$ which exhibit moderate catalytic activity for ethylene copolymerization with 1hexene 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-dimethylaniline-amido ligand with the general formula Cp*ZrCl₂[ortho-(RNCH₂) $(Me_2N)C_6H_4$ [R = 2,6-Me_2C_6H_3 (1), 2,6-^{*i*}Pr_2C_6H_3 (2), ^{*i*}Pr (3), ^tBu (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^{-*i*}Pr₂C₆H₃ (HLb), ^{*i*}Pr (HLc), ^{*i*}Bu (HLd)] were synthesized according to a literature precedure.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*-

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Scheme 1 The synthetic procedure of complexes 1–4.

 $(Me_2N)C_6H_4CH_2NHR$ with 1 equiv of ^{*n*}BuLi 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 HLc (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-^{*i*}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 upfield from those in the corresponding free ligands (2.72 and 2.73 ppm for HLa and HLb, respectively), while the resonances for the NMe_2 protons in complexes 3 (2.69 ppm) and 4 (2.71 ppm) are almost the same as those in the free ligands HLc (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-^{*i*}Pr₂C₆H₃ group about the N–C bond.^{15p,23,25}

It was noticed that the N–*CH*₂ 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, ${}^{2}J_{H-H} = 16$ 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–*CH*₂ protons was



Fig. 1 Variable-temperature ¹H NMR spectra of complex 4 in CDCl₃.



Scheme 2 Possible dynamic processes which may be responsible for the phenomena observed in the variable-temperature ¹H NMR experiments with complex 4.

observed for complexes 1-3 in similar variable-temperature ¹H NMR experiments. In addition, the resonance of the NMe_2 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 $P2_1/C$ while complex 4 crystallizes in a triclinic system with space group $P\overline{1}$. Complexes 1–4 all have a pseudo-tetrahedral coordination environment around their metal centers in the solid state



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 (°): $Cp^*(cent)-Zr(1) = 2.202$, Zr(1)-N(1) = 2.0177(18), Zr(1)-Cl(1) = 2.4155(6), Zr(1)-Cl(2) = 2.4149(6), Cl(1)-Zr(1)-Cl(2) = 107.10(2), N(1)-Zr(1)-Cl(1) = 104.46(5), N(1)-Zr(1)-Cl(2) = 106.13(5), C(11)-N(1)-Zr(1) = 143.53(15), C(19)-N(1)-Zr(1) = 101.65(13), C(11)-N(1)-Cl(2) = 111.2, $Cp^*(cent)-Zr(1)-N(1) = 116.6$.



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 (°): $Cp^*(cent)-Zr(1) = 2.220$, Zr(1)-N(1) = 2.040(9), Zr(1)-Cl(1) = 2.387(4), Zr(1)-Cl(2) = 2.410(4), Cl(1)-Zr(1)-Cl(2) = 105.30(17), N(1)-Zr(1)-Cl(1) = 103.9(3), N(1)-Zr(1)-Cl(2) = 103.0(3), C(11)-N(1)-Zr(1) = 124.9(7), C(23)-N(1)-Zr(1) = 121.1(7), C(11)-N(1)-Cl(2) = 113.7(8), $Cp^*(cent)-Zr(1)-Cl(1) = 109.9$, $Cp^*(cent)-Zr(1)-Cl(2) = 109.2$, $Cp^*(cent)-Zr(1)-N(1) = 123.9$.

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 Cp*MCl₂[N(2,6-R₂C₆H₃)(CH₃)] (M = Ti, Zr; R = Me, ⁱPr),^{15p,23} 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



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 (°): $Cp^*(cent)-Zr(1) = 2.198$, Zr(1)-N(1) = 2.007(2), Zr(1)-Cl(1) = 2.4221(7), Zr(1)-Cl(2) = 2.4198(7), Cl(1)-Zr(1)-Cl(2) = 104.80(3), N(1)-Zr(1)-Cl(1) = 109.05(6), N(1)-Zr(1)-Cl(2) = 103.25(6), C(11)-N(1)-Zr(1) = 144.40(17), C(20)-N(1)-Zr(1) = 100.35(15), C(11)-N(1)-Cl(2) = 115.2(2), $Cp^*(cent)-Zr(1)-Cl(1) = 110.9$, $Cp^*(cent)-Zr(1)-Cl(2) = 112.7$, $Cp^*(cent)-Zr(1)-N(1) = 115.4$.



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 (°): $Cp^*(cent)-Zr(1) = 2.216$, Zr(1)-N(1) = 2.0218(16), Zr(1)-Cl(1) = 2.4180(5), Zr(1)-Cl(2) = 2.4231(5), Cl(1)-Zr(1)-Cl(2) = 100.18(2), N(1)-Zr(1)-Cl(1) = 102.42(5), N(1)-Zr(1)-Cl(2) = 107.45(5), C(11)-N(1)-Zr(1) = 101.86(11), C(20)-N(1)-Zr(1) = 140.00(12), C(11)-N(1)-Cl(2) = 117.19(15), $Cp^*(cent)-Zr(1)-Cl(1) = 110.6$, $Cp^*(cent)-Zr(1)-Cl(2) = 111.3$, $Cp^*(cent)-Zr(1)-N(1) = 122.1$.

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 (2.4210 Å) and 4 (2.4206 Å) are close to those reported in complexes $Cp*ZrCl_2[N(2,6-R_2C_6H_3)]$ (CH₃)] (R = i Pr, 2.414 Å; R = Me, 2.403 Å).²³ The Cp*(cent)– Zr distances in complexes 1 (2.202 Å), 2 (2.220 Å), 3 (2.198 Å) and 4 (2.216 Å) are close to those reported in complexes $Cp*ZrCl_{2}[N(2,6-R_{2}C_{6}H_{3})(CH_{3})]$ (R = ^{*i*}Pr, 2.197 Å; R = Me, 2.214 Å).²³ The Cl(1)-Zr(1)-Cl(2) angles in these complexes decrease in the order of 1 $(107.10^{\circ}) > 2(105.30^{\circ}) > 3 (104.80) >$ 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 Cp*(cent)–Zr(1)–N(1) angles in complex 2 (123.9°) and complex 4 (122.1°) are larger than those in complexes 1 (116.6°) and 3 (115.4°), which is obviously caused by the bulky N-R group in the former complexes.

Table 1 A summary of ethylene polymerization catalyzed by 1–4/AlⁱBu₃/Ph₃CB(C₆F₅)₄ systems^a

Run	Catalyst	<i>T</i> /°C	Al/Zr mol ratio	Yield (g)	Activity ^b	$M_{\rm w}{}^{c} \times 10^{-4}$	$M_{ m w}/M_{ m n}^{\ c}$	$T_{\rm m}^{\ \ d}(^{\circ}{\rm C})$
1	1	80	350	0.971	1942	12.4	2.09	138.3
2	2	80	350	0.742	1482	8.69	2.45	137.9
3	3	80	350	1.032	2064	12.2	2.24	139.3
4	4	60	250	0.404	808	7.91	2.26	139.8
5	4	80	250	0.772	1544	7.60	2.04	139.7
6	4	80	350	1.135	2270	6.79	2.25	137.8
7	4	100	350	0.845	1690	3.45	2.10	138.6
8	4	80	450	0.880	1760	3.60	2.22	137.9

^{*a*} Polymerization conditions: toluene 70 mL, catalyst 2 μ mol 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. ^{*d*} Determined by DSC at a heating rate of 10 °C min⁻¹ and the data from the second scan are used.

Table 2 A summary of ethylene/1-hexene copolymerization catalyzed by $1-4/Al^iBu_3/Ph_3CB(C_6F_5)_4$ systems^a

Run	Catalyst	Yield (g)	Activity ^b	1-hexene content ^c (mol%)	$M_{\rm w}^{\ \ d} \ge 10^{-4}$	$M_{\rm w}/M_{\rm n}^{\ d}$	$T_{\rm m}^{\ e}(^{\circ}{\rm C})$
1	1	0.847	1694	3.22	11.4	3.51	128.4
2	2	0.825	1650	3.00	7.69	3.34	128.9
3	3	1.004	2008	0.55	10.2	3.68	129.2
4	4	1.155	2310	3.76	5.81	3.12	127.2

^{*a*} Polymerization conditions: toluene + 1-hexene total 70 mL, catalyst 2 μ mol 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*} Calculated based on ¹³C NMR spectra. ^{*d*} Determined by GPC in *o*-dicholobenzene *vs.* polystyrene standard. ^{*e*} Determined by DSC at a heating rate of 10 °C min⁻¹ and the data from the second scan are used.

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 AlⁱBu₃ 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 was also examined at different polymerization temperatures and the maximal values were observed around 80 °C. The molecular weight of the obtained polyethylenes by these catalysts is moderate ($M_{\rm w}$ = $3.6-13.0 \times 10^4$ g mol⁻¹). As expected, the molecular weight of the polyethylenes decreases with the increase in the Al/Zr molar ratio and the elevation in polymerization temperature, due to the acceleration of the chain transfer reaction to alkylaluminum in the former case and the decrease in the concentration of ethylene in toluene with increasing the polymerization temperature in the latter case. In addition, the melting temperatures of the obtained polyethylenes are in the range of 136-140 °C, being typical for linear polyethylene

Copolymerization of ethylene with 1-hexene with complexes 1–4 as precatalysts was also explored and the copolymerization results are summarized in Table 2. The catalytic activity of these catalysts for the ethylene/1-hexene copolymerization under similar conditions changes in the same order as observed in the

ethylene homopolymerization reaction: 4 > 3 > 1 > 2. The obtained poly(ethylene-co-1-hexene)s were analyzed by ¹³C NMR and GPC. Based on the ¹³C NMR analysis,²⁶ the comonomer content in the poly(ethylene-co-1-hexene)s was calculated and the data are listed in Table 2. It can be seen from these results that the comonomer incorporation ability 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.²⁷ 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 (M_w = $6.8-12.0 \times 10^4$ 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 $Cp*ZrCl_2[ortho-(RNCH_2)(Me_2N)C_6H_4]$ were synthesized by the reaction of $Cp*ZrCl_3$ 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. 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 pseudotetrahedral 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 Al^{*i*}Bu₃/Ph₃CB(C₆F₅)₄, 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)s 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. $Cp*ZrCl_3$,²⁸ HLa, HLb, *ortho*-C₆H₄(NMe)₂CHO²⁴ and Ph₃CB(C₆F₅)₄²⁹ were prepared according to literature procedures. Polymerization grade ethylene was further purified by passage through columns of 5 Å molecular sieves and MnO. AlⁱBu₃, ⁿBuLi, and ZrCl₄ were purchased from Aldrich or Acros. ¹H 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 1,2,4trichlobenzene 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.

of ortho-C₆H₄NMe₂CH₂NHⁱPr (HLc). ortho-Synthesis $C_6H_4(NMe)_2CHO$ (2.24 g, 15.0 mmol) and ^{*i*}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 stirred and heated to reflux for 8 h. The solvent was removed under reduced pressure to leave the Schiff base product ortho-C₆H₄NMe₂CH=NⁱPr as an orange oil (2.71 g, 14.3 mmol, 95%). ¹H NMR (CDCl₃, 300 MHz, 298 K): δ 8.61 (s, 1 H, CH = N), 7.84 (d, 1 H, ArH, ${}^{3}J_{H-H} = 7.2$ Hz), 7.33 (t, 1 H, Ar*H*, ${}^{3}J_{H-H} = 7.5$ Hz), 7.03 (d, 1 H, Ar*H*, ${}^{3}J_{H-H} = 7.5$ Hz), 7.02 (t, 1 H, ArH, ${}^{3}J_{H-H} = 7.2$ Hz), 3.58 (sept, 1 H, CHMe₂, ${}^{3}J_{\text{H-H}} = 6.3 \text{ Hz}$, 2.76 (s, 6 H, N(CH₃)₂), 1.27 (d, 6 H, CHMe₂, ${}^{3}J_{\text{H-H}} = 6.3$ Hz) ppm. The Schiff base compound was dissolved in THF (50 mL). To the solution was slowly added 0.542 g of LiAlH₄ (14.3 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred over night. The reaction was quenched with 20 mL of water and the insoluble solids were 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 and concentrated by distillation under reduced pressure to give the final product HLc (2.44 g, 12.7 mmol, 89%) as an orange oil. ¹H NMR (CDCl₃, 300 MHz, 298 K): δ 7.29 (d, 1 H, Ar*H*, ³*J*_{H-H} = 7.5 Hz), 7.21 (t, 1 H, Ar*H*, ³*J*_{H-H} = 8.1 Hz), 7.10 (d, 1 H, Ar*H*, ³*J*_{H-H} = 8.1 Hz), 7.02 (t, 1 H, Ar*H*, ³*J*_{H-H} = 7.8 Hz), 3.85 (s, 2 H, NC*H*₂), 2.78 (sept, 1 H, C*H*Me₂, ³*J*_{H-H} = 6.3 Hz), 2.70(s, 6 H, N(C*H*₃)₂), 1.93 (br, 1 H, N*H*), 1.08 (d, 6 H, CH*Me*₂, ³*J*_{H-H} = 6.0 Hz) ppm. ¹³C NMR(CDCl₃, 75 MHz, 298 K): δ 152.6, 135.0, 129.7, 127.4, 123.2, 119.3, 48.0, 47.9, 44.9, 22.9 ppm.

Synthesis of *ortho*-C₆H₄NMe₂CH₂NH'Bu (HLd). HLd was synthesized using a procedure identical to that for HLc 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=N'Bu (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, ³J_{H-H} = 7.8 Hz), 7.32 (t, 1 H, ArH, ³J_{H-H} = 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. ¹H NMR (CDCl₃, 300 MHz, 298 K): δ 6.98–7.36 (m, 4 H, ArH), 3.79 (s, 2 H, NCH₂), 2.71(s, 6 H, N(CH₃)₂), 1.18 (s, 9 H, 'Bu) 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.

Lithium salt of ligand *ortho*-C₆H₄NMe₂CH₂NH(2,6-Me₂-C₆H₃) (LiLa). 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 over night. The resultant precipitates were collected on a frit, washed with *n*-hexane, and dried under vacuum to give LiLa in a yield of 83% (1.63 g, 6.27 mmol).

Lithium salts LiLb, LiLc, and LiLd were prepared in the same way as described above for LiLa

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, Ar*H*, ³*J*_{H-H} = 7.5 Hz), 7.14 (t, 1 H, Ar*H*, ${}^{3}J_{\text{H-H}} = 7.5 \text{ Hz}$), 6.98 (t, 1 H, Ar*H*, ${}^{3}J_{\text{H-H}} = 7.5 \text{ Hz}$), 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, CpMe₅), 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, 18.4, 11.3 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

Complexes	1	2	3	4
Formula	C27H36Cl2N2Zr	C31H44Cl2N2Zr	C22H34Cl2N2Zr	C23H36Cl2N2Zr
Fw	550.70	606.80	488.63	502.66
Wavelength(Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_{1}/c$	$P2_1/c$	$P2_1/c$	$P\overline{1}$
a/Å	8.5545(5)	20.13(2)	10.2590(6)	8.0251(6)
b/Å	13.5020(8)	8.833(10)	14.6848(8)	11.4954(8)
c/Å	23.1132(14)	19.65(2)	16.2009(9)	13.8983(10)
α (°)	90	90	90	105.0150(10)
β (°)	93.1080(10)	116.601(15)	100.5010(10)	94.0820(10)
γ (°)	90	90	90	98.1910(10)
V/\dot{A}^3	2665.7(3)	3125(6)	2399.8(2)	1217.87(15)
Ζ	4	4	4	2
<i>F</i> (000)	1144	1272	1016	524
$Dc/g cm^{-3}$	1.372	1.290	1.352	1.371
μ/mm^{-1}	0.630	0.544	0.690	0.682
θ range (deg)	1.75-26.03	2.07-25.25	1.89-25.04	1.86-26.03
No. of reflns	16223	27146	13582	7365
No. of indep. reflns	5247	5539	4227	4682
R(int)	0.0311	0.1307	0.0290	0.0113
Data/restraints/parameters	5247/2/306	5539/12/337	4227/1/257	4682/0/263
GOF	1.030	1.131	1.048	1.037
$R_1, R_W [I > 2\sigma(I)]$	0.0325, 0.0737	0.1051, 0.2428	0.0320, 0.0730	0.0260, 0.0658
R_1, Rw (all data)	0.0413, 0.0782	0.1605, 0.2709	0.0432, 0.0775	0.028, 0.0675
Max(min) diff peak/e $Å^{-3}$	0.370, -0.240	0.987, -1.436	0.477, -0.207	0.338, -0.311

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as orange crystals. Anal. Calcd. for $C_{31}H_{44}Cl_2N_2Zr(606.80)$: 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, ³J_{H-H} = 6.6 Hz), 2.18 (s, 15 H, CpMe₅), 2.16 (s, 6 H, N(CH₃)₂), 1.23 (d, 6 H, CH(CH₃)₂, ³J_{H-H} = 6.6 Hz), 0.71 (d, 6 H, CH(CH₃)₂, ³J_{H-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 mmol, 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, Ar*H*), 4.67 (s, 2H, NC*H*₂), 4.60 (sept, 1 H, C*H*(CH₃)₂, ³*J*_{H-H} = 6.0 Hz), 2.69 (s, 6 H, N(C*H*₃)₂), 2.07 (s, 15 H, Cp*Me*₅), 1.07 (d, 6 H, CH (C*H*₃)₂, ³*J*_{H-H} = 6.0 Hz) ppm. ¹³C NMR (CDCl₃, 75 MHz, 298 K): *δ* 135.9, 128.2, 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 mmol, 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, Ar*H*, ³*J*_{H-H} = 7.5 Hz), 7.19 (t, 1 H, Ar*H*, ³*J*_{H-H} = 7.2 Hz), 7.09 (d, 1 H, Ar*H*, ³*J*_{H-H} = 7.5 Hz), 7.02(t, 1 H, Ar*H*, ³*J*_{H-H} = 7.2 Hz), 4.23 (s, 2 H, NCH₂), 2.71(s, 6 H, N(CH₃)₂), 2.18 (s, 15 H, Cp*Me*₅), 1.05 (s, 9 H, ^tBu) 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/*n*-hexane (v/v = 1–2:10) mixed solvent system. The data were collected on a Rigaku RAXIS-RAPID diffractometer with Mo-K α (λ = 0.71073 Å) radiation. All structures were solved by direct method³⁰ 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.³¹ 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, thermostated at a desired temperature and saturated with ethylene (1.0 atm). The polymerization reaction was started by addition of a mixture of catalyst and AlⁱBu₃ 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.

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Notes and references

- 1 G. W. Coates and R. M. Waymouth, Science, 1995, 267, 217.
- 2 A. L. McKnight and R. M. Waymouth, Chem. Rev., 1998, 98, 2587.
- 3 H. G. Alt and A. Köppl, Chem. Rev., 2000, 100, 1205.
- 4 H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143.
- 5 R. J. Long, V. C. Gibson and A. J. P. White, *Organometallics*, 2008, 27, 235.
- 6 (a) K. Nomura, J. Liu, S. Padmanabhan and B. Kitiyanan, J. Mol. Catal. A: Chem., 2007, 267, 1; (b) K. Nomura, Dalton Trans., 2009 (41), 8811.
- T. L. Iaao, L. Caporaso, G. Senatore and L. Oliva, *Macromolecules*, 1999, 32, 6913.
- 8 (a) Y. Obora, C. L. Stern, T. J. Marks and P. N. Nickias, Organometallics, 1997, 16, 2503; (b) N. Schneider, M. E. Huttenloch, U. Stehling, R. Kirsten, F. Schaper and H. H. Brintzinger, Organometallics, 1997, 16, 3413; (c) A. J. Puranen, M. Klinga, M. Leskelä and T. Repo, Organometallics, 2004, 23, 3759.
- 9 (a) Y.-X. Chen and T. J. Marks, Organometallics, 1997, 16, 3649;
 (b) R. Goretzki and G. Fink, Macromol. Rapid Commun., 1998, 19, 511;
 (c) H. Hagihara, K. Tsuchihara, K. Takeuchi, M. Murata, H. Ozaki and T. Shiono, J. Polym. Sci., Part A: Polym. Chem., 2004, 42, 52.
- 10 (a) E. Hauptman, R. M. Waymouth and J. Ziller, J. Am. Chem. Soc., 1995, 117, 11586; (b) S. Lin and R. M. Waymouth, Acc. Chem. Res., 2002, 35, 765.
- 11 (a) Y. X. Chen, M. D. Rausch and J. C. W. Chien, *Macromolecules*, 1995, **28**, 5399; (b) D. M. Shin, V. H. Pham, K. W. La, I. K. Song and J. S. Chung, *Res. Chem. Intermed.*, 2008, **34**, 687.
- (a) L. Izzo, M. Napoli and L. Oliva, *Macromolecules*, 2003, 36, 9340;
 (b) L. Caporaso, L. Izzo, I. Sisti and L. liva, *Macromolecules*, 2002, 35, 4866.
- (a) R. Quijada, J. L. Guevara, G. B. Galland, F. M. Rabagliati and J. M. Lopez-Majada, *Polymer*, 2005, 46, 1567; (b) J. W. Zhang, B.-G. Li, H. Fan and S. P. Zhu, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, 45, 3562; (c) H. Lasarov, K. Mönkkönen and T. T. Pakkanen, *Macromol. Chem. Phys.*, 1998, 199, 1939.
- (a) L. Resconi, R. L. Jones, A. L. Rheingold and G. P. A. Yap, Organometallics, 1996, 15, 998; (b) L. Resconi, R. L. Jones, E. Albizzati, I. Camurati, F. Piemontesi, F. Guglielmi and G. Balbontin, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.), 1994, 35, 663.
- (a) J. A. M. Canich, G. G. Hlatky, H. W. Turner, US Pat., 542236, 1990;
 (b) J. A. M. Canich, US Pat., 5026789, 1991; (c) J. A. M. Canich, Eur. Pat. Appl., 420436, 1991; (d) J. C. Stevens, F. J. Timmers, D. R. Wilson, G. F. Schmidt, P. N. Nickias, R. K. Rosen, G. W. Knight, S. -Y. Lai, Eur. Pat. Appl., 416815, 1991; (e) J. C. Stevens, D. R. Nelthamer, Eur. Pat. Appl., 418022, 1991; (f) D. D. Devore, F. J. Timmers, D. L. Hasha, R. K. Rosen, T. J. Maks, P. A. Deck and C. L. Stern, Organometallics, 1995, 14, 3132; (g) K. E. du Plooy, U. Moll, S. Wocadlo, W. Massa and J. Okuda, Organometallics, 1995, 14, 3129; (h) D. W. Carpenetti, L. Kloppenburg, J. T. Kupec and J. L. Petersen,

Organometallics, 1996, 15, 1572; (i) A. L. MacKnight, M. A. Masood, R. M. Waymouth and D. A. Straus, Organometallics, 1997, 16, 2879; (j) K. Nomura, N. Naga, M. Miki, K. Yanagi and A. Imai, Organometallics, 1998, 17, 2152; (k) K. Nomura, K. Oya, T. Komatsu and Y. Imanishi, Macromolecules, 2000, 33, 3187; (l) K. Nomura, K. Itagaki and M. Fujiki, Macromolecules, 2005, 38, 2053; (m) K. Nomura, J. Liu, M. Fujiki and A. Takemoto, J. Am. Chem. Soc., 2007, 129, 14170; (n) K. Nomura and K. Fujii, Macromolecules, 2003, 36, 2633; (o) P. J. Sinnema, T. P. Spaniol and J. Okuda, J. Organomet. Chem., 2000, 598, 179; (p) K. Liu, Q. Wu, W. Gao, Y. Mu and L. Ye, Eur. J. Inorg. Chem., 2011, 1901.

- 16 (a) R. Gòmez, R. Duchateau, A. N. Chernega, J. H. Teuben, F. T. Edelmann and M. L. H. Green, J. Organomet. Chem., 1995, 491, 153.
- (a) A. Antiñolo, F. Carrillo-Hermosilla, A. Corrochano, J. Fernández-Baeza, A. Lara-Sanchez, M. R. Ribeiro, M. Lanfranchi, A. Otero, M. A. Pellinghelli, M. F. Portela and J. V. Santos, *Organometallics*, 2000, **19**, 2837; (b) J.-Y. Liu, S. R. Liu, B. X Li, Y.-G. Li and Y.-S. Li, *Organometallics*, 2011, **30**, 4052.
- 18 (a) R. K. J. Bott, D. L. Hughes, M. Schormann, M. Bochmann and S. J. Lancaster, J. Organomet. Chem., 2003, 665, 135; (b) W. Huang, X. Sun, H. Ma and J. Huang, Inorg. Chim. Acta., 2010, 363, 2009.
- 19 (a) A. R. Cabrera, Y. Schneider, M. Valderrama, R. Fröhlich, G. Kehr, G. Erker and R. S. Rojas, *Organometallics*, 2010, **29**, 6104; (b) R. Vallmerhaus, M. Rahim, R. Tomaszewski, S. Xin, N. J. Taylor and S. Collins, *Organometallics*, 2000, **19**, 2161.
- 20 P. Hu, F. Wang and G.-X. Jin, Organometallics, 2011, 30, 1008.
- 21 (a) S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa and T. Fujita, J. Am. Chem. Soc., 2001, **123**, 6847; (b) T. Matsugi and T. Fujita, Chem. Soc. Rev., 2008, **37**, 1264.
- 22 (a) S.-D. Bai, H. Tong, J. Guo, M.-S. Zhou, D.-S. Liu and S.-F. Yuan, *Polyhedron*, 2010, 29, 262; (b) M.-S. Zhou, S. Zhang, H. Tong, W.-H. Sun and D.-S. Liu, *Inorg. Chem. Commun.*, 2007, 10, 1262; (c) S.-F. Yuan, S.-D. Bai, D.-S. Liu and W.-H. Sun, *Organometallics*, 2010, 29, 2132; (d) S.-F. Yuan, X. Wei, H. Tong, L., Zhang, D.-S. Liu and W.-H. Sun, *Organometallics*, 2010, 29, 2085.
- 23 K. Liu, Q Wu, W Gao and Y Mu, Dalton Trans., 2011, 40, 4715.
- 24 A. Gao, Y. Mu, J. Zhang and W. Yao, Eur. J. Inorg. Chem., 2009, 3613.
- 25 (a) P. G. Hayes, G. C. Welch, D. J. H. Emslie, C. L. Noack, W. E. Piers and M. Parvez, *Organometallics*, 2003, **22**, 1577; (b) J. D. Scollard, D. H. McConville, N. C. Payne and J. J. Vittal, *Macromolecules*, 1996, **29**, 5241.
- 26 J. C. Randall, J. Macromol. Sci. Rev. Macromol. Chem. Phys., 1989, C29 (2&3), 201.
- (a) K. Nomura, K. Fujita and M. Fujiki, J. Mol. Catal. A: chem., 2004,
 220, 133; (b) D. J. Cho, C. J. Wu, S. S, W.-S. Han, S. O. Kang and B. Y. Lee, Organometallics, 2006, 25, 2133.
- 28 P. T. Wolczanski and J. E. Bercaw, Organometallics, 1982, 1, 793.
- (a) A. G. Massey and A. J. Park, J. Organomet. Chem., 1964, 2, 245;
 (b) A. G. Massey and A. J. Park, J. Organomet. Chem., 1966, 5, 218;
 (c) J. C. W. Chien, W. M. Tsai and M. D. Rasch, J. Am. Chem. Soc., 1991, 113, 8570.
- 30 SMART and SAINT software packages, Siemens Analytical X-ray instruments, Inc., Madison, WI, 1996
- 31 G. M. Sheldrick, SHELXTL, Version 5.1, Siemens Industrial Automation, Inc., 1997