Dalton
Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 4715

www.rsc.org/dalton

PAPER

Half-zirconocene anilide complexes: synthesis, characterization and catalytic properties for ethylene polymerization and copolymerization with 1-hexene†

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Received 17th December 2010, Accepted 16th February 2011
DOI: 10.1039/c0dt01789b

A number of half-zirconocene anilide complexes of the type Cp*ZrCl$_2$[N(2,6-R$^1_2$C$_6$H$_3$)R^2] [R^1 = ^{i}Pr (**1**, **3**), Me (**2**); R^2 = Me (**1**, **2**), Bn (**3**)] and Cp*ZrCl[N(2,6-Me$_2$C$_6$H$_3$)Me]$_2$ (**4**) (Cp* = pentamethylcyclopentadienyl) were synthesized from the reactions of Cp*ZrCl$_3$ with the lithium salts of the corresponding anilide in diethyl ether at room temperature. All new zirconium complexes were characterized by ^{1}H and ^{13}C NMR and elemental analysis. Molecular structures of complexes **1**, **2** and **4** were determined by single crystal X-ray diffraction analysis. Upon activation with Al^{i}Bu$_3$ and Ph$_3$CB(C$_6$F$_5$)$_4$, complexes **1–4** exhibit good catalytic activity for ethylene polymerization, and produce polyethylene with a moderate molecular weight. Among these zirconium complexes, complex **1** shows the highest catalytic activity while complex **4** shows the lowest catalytic activity for ethylene polymerization. Complexes **1–3** also exhibit moderate catalytic activity for copolymerization of ethylene with 1-hexene, and produce copolymers with relatively high molecular weight and reasonable 1-hexene incorporation. In addition, the activation procedure of these catalyst systems were studied by ^{1}H NMR spectroscopy.

Introduction

Since Sinn and Kaminsky discovered that metallocene complexes show high catalytic activity for ethylene polymerization when activated with methylaluminoxane (MAO),[1] group 4 metallocene complexes have attracted great interest both in academic and industrial institutes due to their excellent performance as catalysts in the production of polyolefin materials with tailored structures and properties.[2–7] To develop new metallocene catalysts with good catalytic performance, a large number of group 4 metallocene complexes have been synthesized.[2,8–10] As one of the most efficient catalyst types for olefin polymerization, zirconocene complexes have been widely studied for ethylene[11] and propylene[1,5,12] polymerization and copolymerization with higher α-olefins.[13] Some non-bridged and bridged zirconocene complexes have been found to exhibit unique catalytic characteristics for the stereospecific polymerization of propylene.[14–18] Since constrained geometry and non-bridged monocyclopentadienyl titanium complexes have been known to be good catalysts for ethylene copolymerization with α-olefins,[19] some non-bridged monocyclopentadienyl zirconium complexes bearing a benzamidinate,[20] aryloxy,[21] salicylaldiminato[22] or β-diketiminate[23] ligand were also synthesized and tested as catalysts for ethylene polymerization and copolymerization with α-olefins. So far, only a few number of zirconium complexes of this type with an amide ligand have been reported,[24] and none of them have been studied as catalysts for ethylene–α-olefin copolymerization. We have recently found that non-bridged monocyclopentadienyl titanium complexes with an anilide ligand show good catalytic properties for ethylene–1-hexene copolymerization.[25] It is therefore of interest to develop the analogous zirconium complexes of this type and investigate their catalytic performance for ethylene polymerization and ethylene–α-olefin copolymerization. In this contribution, we report the synthesis and characterization of several half-zirconocene anilide complexes of the type Cp*ZrCl$_2$[N(2,6-R$^1_2$C$_6$H$_3$)R^2] [R^1 = ^{i}Pr(**1**, **3**), Me(**2**); R^2 = Me(**1**, **2**), Bn(**3**)] and Cp*TiCl[N(2,6-Me$_2$C$_6$H$_3$)Me]$_2$ (**4**) (Cp* = pentamethylcyclopentadienyl), and their catalytic performance for ethylene homopolymerization and copolymerization with 1-hexene.

Results and discussion

Synthesis and characterization of new compounds

The aniline free ligands HN(2,6-R$^1_2$C$_6$H$_3$)R^2 [R^1 = ^{i}Pr (**HLa**, **HLc**), Me (**HLb**), R^2 = Me (**HLa**, **HLb**), Bn (**HLc**)] were synthesized according to previously reported procedures.[25,26] The free ligands **HLa** and **HLb** were synthesized in high yields (>85%) from the reaction of CH$_3$I with a corresponding lithium 2,6-R$^1_2$-anilide obtained by treating the corresponding 2,6-R$^1_2$-aniline with ^{n}BuLi. The free ligand **HLc** was synthesized in a high yield of

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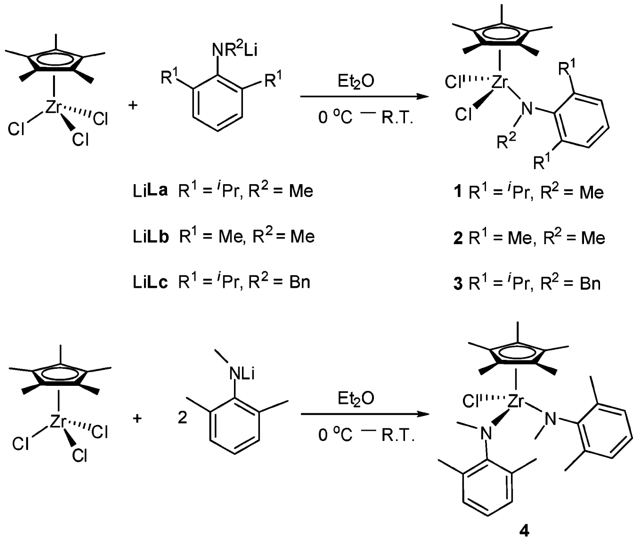
† Electronic supplementary information (ESI) available. CCDC reference numbers 804798–804800. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01789b

about 80% by a two step procedure: a condensation reaction of benzaldehyde with 2,6-diisopropylaniline, followed by reduction of the formed Schiff base compound with $LiAlH_4$. Complexes **1–3** were synthesized in high yields (65–80%) according to a published procedure[24,27] by reactions of Cp^*ZrCl_3 in diethyl ether with 1 equiv of the corresponding $LiN(2,6\text{-}R^1{}_2C_6H_3)R^2$ [R^1 = ^{i}Pr (Li**La**, Li**Lc**), Me (Li**Lb**); R^2 = Me (Li**La**, Li**Lb**), Bn (Li**Lc**)], respectively (Scheme 1). The bisanilide zirconium complex **4** was obtained from the reaction of Cp^*ZrCl_3 with 2 equiv of $LiN(2,6\text{-}Me_2C_6H_3)Me$ in a yield of 75%. Complexes **1–4** are quite soluble in methylene chloride, toluene, benzene, and diethyl ether, but less soluble in *n*-pentane and *n*-hexane. These complexes were all characterized by ^1H and ^{13}C NMR spectroscopy along with elemental analysis. The ^1H NMR spectra of complexes **1** and **3** show two set of doublets for the methyl protons of the $CH(CH_3)_2$ group (1.14 and 1.33 ppm for **1**; 0.59 and 1.22 ppm for **3**), and the ^{13}C NMR spectra of both complexes show two signals for the two methyl groups (27.0 and 27.2 ppm for **1**; 25.0 and 25.9 ppm for **3**) of the ^{i}Pr group in these complexes, indicating that the rotation of the $2,6\text{-}^iPr_2C_6H_3$ group about the N–C (Ar group) bond is restricted.[25,28] The ^1H NMR signal for the N–*Me* protons in the two anilide ligands of complex **4** shifts about 0.6 ppm toward higher field compared to the corresponding signal in complex **2** with one anilide ligand.



Scheme 1 Synthetic procedure of complexes **1–4**.

Crystal structures of complexes 1, 2 and 4

Molecular structures of complexes **1**, **2** and **4** were determined by single crystal X-ray diffraction analysis. The ORTEP drawings of their molecular structures are shown in Fig. 1, 2 and 3, respectively. The selected bond lengths and angles are summarized in Table 1. The molecular structural analysis reveals that all the complexes **1**, **2** and **4** have a pseudo-octahedral coordination environment in their solid state and adopt a three-legged piano stool geometry with the anilide N and Cl atoms being the three legs and the Cp* ring being the seat. The aryl ring in the anilide ligand in complexes **1** and **2** is almost parallel to the Cp* ring with the $N–CH_3$ group directed away from the cyclopentadienyl ring. In the case of complex **4**, the aryl ring in one anilide ligand is approximately parallel to the Cp* ring, with an angle of 11.7°, while the aryl ring in another anilide ligand is nearly perpendicular to the Cp* ring, with an angle of 84.7°. The Zr–N distances in complexes **1** and **2** are somewhat shorter than the ones in complex **4** and those previously reported in the complex $[(2,6\text{-}^iPr_2C_6H_3)(SiMe_3)N]_2ZrCl_2$ (2.029, 2.030 Å).[24b] The average Zr–Cl distances in complexes **1** (2.4144 Å), **2** (2.4030 Å) and **4** are in line with the one in $CpZrCl_2[\eta^3\text{-}CPh(NSiMe_3)_2]$ (2.422 Å),[20] but longer than that in $[(2,6\text{-}^iPr_2C_6H_3)(SiMe_3)N]_2ZrCl_2$ (2.380 Å). The Cp*(cent)–Zr distances in complexes **1** and **2** are shorter than that in the more crowded complex **4**. The Cl–Zr–Cl angles in complexes **1** and **2** are larger than those reported for $CpZrCl_2[\eta^3\text{-}CPh(NSiMe_3)_2]$ (90.95°)[20] and a hafnium analogue $Cp^*HfCl_2[N(2,6\text{-}^iPr_2C_6H_3)SiMe_3]$ (101.9°).[24b] The Cp*(cent)–Zr–Cl angles in complexes **1** and **2** are slightly larger than that in complex **4**. The two Cp*(cent)–Zr–N angles in complex **4** are quite different with one being smaller, but the other being larger than those in complexes **1** and **2**. The Zr–N–C(phenyl) angles in complexes **1** and **2** are larger than those in complex **4**, probably due to the larger repulsion between the two anilide ligands in the latter complex.

Table 1 Selected bond lengths (Å) and angles (deg) for complexes **1**, **2** and **4**

Complexes	1	2	4
Zr(1)–N(1)	2.0141(15)	1.998(3)	2.032(4)
Zr(1)–N(2)	—	—	2.051(4)
Zr(1)–Cl(1)	2.4147(5)	2.3890(15)	2.4398(12)
Zr(1)–Cl(2)	2.4141(5)	2.4171(15)	—
Zr(1)–Cp*(cent)	2.197	2.214	2.258
Cl(1)–Zr(1)–Cl(2)	106.51(2)	106.36(6)	—
N(1)–Zr(1)–Cl(1)	104.74(5)	103.52(10)	103.02(11)
N(2)–Zr(1)–Cl(1)	—	—	99.06(11)
N(1)–Zr(1)–N(2)	—	—	105.99(14)
N(1)–Zr(1)–Cl(2)	104.30(5)	103.42(10)	—
Zr(1)–N(1)–C(11)	100.44(12)	104.2(2)	106.3(3)
Zr(1)–N(1)–C(12)	146.35(13)	144.2(3)	142.5(3)
Zr(1)–N(2)–C(20)	—	—	115.9(3)
Zr(1)–N(2)–C(21)	—	—	132.2(3)
Cp*(cent)–Zr(1)–Cl(1)	112.2	113.3	109.0
Cp*(cent)–Zr(1)–Cl(2)	111.5	113.8	—
Cp*(cent)–Zr(1)–N(1)	116.8	117.3	114.3
Cp*(cent)–Zr(1)–N(2)	—	—	122.8

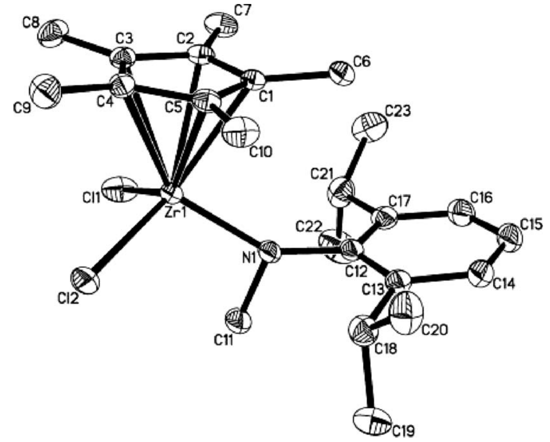


Fig. 1 Perspective view of **1** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity.

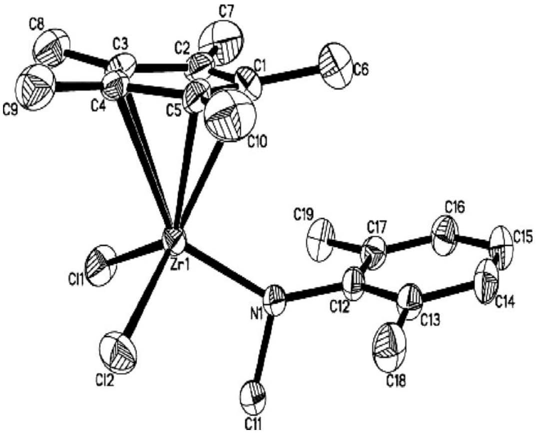


Fig. 2 Perspective view of **2** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity.

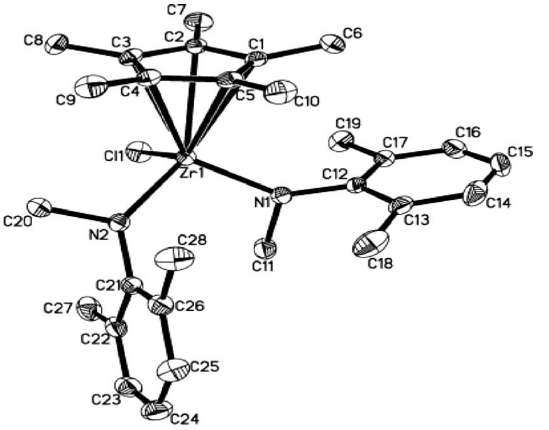


Fig. 3 Perspective view of **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity.

Ethylene polymerization

Ethylene polymerization reactions using complexes **1–4** as precatalysts under different conditions were studied, and the results are summarized in Table 2. Upon activation with Al^{i}Bu$_3$ and Ph$_3$CB(C$_6$F$_5$)$_4$, complexes **1–4** all exhibit good catalytic activity for ethylene polymerization. Under similar conditions, the catalytic activity decreases in the order of **1** > **3** > **2** > **4**, indicating that the catalytic activity of these complexes is influenced by the nature of the substituents on the anilide ligands. It is well known that electron-donating substituents on the ligands can stabilize the catalytically active cationic species and improve the catalytic activity.[29] On the other hand, moderately bulky ligands will weaken the interaction between the cationic catalyst and the anionic cocatalyst species, and therefore enhance the catalytic activity too.[13,30] The complex **4** with two anilide ligands exhibits obviously lower catalytic activity than complex **2** with one anilide ligand under the same conditions. On the basis of current understanding on the reaction mechanism of group 4 metallocene catalyst systems,[21,31] the catalytically active cationic species in the two catalyst systems might be the same. However, the bulky bisanilide complex **4** should be more difficult to activate than complex **2**. The catalytic activity of these catalyst systems is sensitive to the polymerization temperature and Al : Zr molar ratio. The maximal catalytic activity for all four catalyst systems was observed around 60 °C with a Al : Zr molar ratio about 300. The polyethylenes obtained with complexes **1–4** possess moderate molecular weight (Mw = 10–26 × 10^4 g mol^{-1}) with a relatively narrow molecular weight distribution, and the molecular weight values of the resultant polyethylenes are remarkably dependent on the structure of the catalyst. The polyethylenes obtained with complex **3** show the highest molecular weight while those produced with complex **2** have the lowest molecular weight under similar conditions, indicating that the substituents on the anilide ligand play an important role in controlling the length of the growing polymer chain. Based on the present results, it seems that catalysts with a bulkier anilide ligand produce polyethylenes with higher molecular weight. In addition, as reported previously for other catalyst systems, the molecular weight values of the resultant polyethylenes decrease with the increase in the polymerization temperature and Al : Zr molar ratio. The melting points of the resultant polyethylenes range from 138–142 °C, which is typical for linear polyethylene. ^{13}C NMR analysis on the polymer samples proves that the polyethylenes produced by these catalysts are indeed linear with no signals for branches.

Copolymerization of ethylene with 1-hexene

Copolymerization reactions of ethylene with 1-hexene using complexes **1–4** as precatalysts under different conditions were also explored, and the copolymerization results are summarized in Table 3. As observed in the ethylene homopolymerization, the catalytic activity of these catalysts for the ethylene–1-hexene copolymerization under similar conditions also changes in the

Table 2 Summary of ethylene polymerization catalyzed by **1–4**–Al^{i}Bu$_3$–Ph$_3$CB(C$_6$F$_5$)$_4$ systems[a]

Run	Catalyst	Temp (°C)	Al : Zr molar ratio	Yield (g)	Activity[b]	Mw[c] × 10^{-4}	Mw/Mn[c]	T_m[d] (°C)
1	**1**	40	300	0.418	334	19.1	3.17	141.6
2	**1**	60	200	0.381	305	18.1	3.16	140.1
3	**1**	60	300	0.732	586	17.2	2.30	140.9
4	**1**	60	400	0.705	564	10.4	2.26	139.6
5	**1**	80	300	0.508	406	12.2	2.72	138.3
6	**2**	60	300	0.360	288	15.3	2.41	139.2
7	**3**	60	300	0.485	388	25.7	2.35	139.4
8	**4**	60	300	0.258	206	20.1	2.64	139.5

[a] Polymerization conditions: toluene 70 mL, catalyst 1 × 10^{-6} mol, B : Zr molar ratio 1.5, time 15 min, ethylene pressure 5 bar. [b] Activity in g PE (mmol Zr)$^{-1}$ h^{-1} bar^{-1}. [c] Determined by GPC in *o*-dichlorobenzene *vs.* polystyrene standard. [d] Determined by DSC at a heating rate of 10 °C min^{-1}; the data from the second scan are used.

Table 3 Summary of ethylene–1-hexene copolymerization catalyzed by **1–4**–Al^{i}Bu$_3$–Ph$_3$CB(C$_6$F$_5$)$_4$ systems[a]

Run	Catalyst	1-hexene (mol L^{-1})	Yield (g)	Activity[b]	1-hexene content[c] (mol%)	$Mw^d \times 10^{-4}$	Mw/Mn^d	$T_m{}^e$ (°C)
1	**1**	0.4	0.192	768	0.64	15.1	3.29	131.5
2	**1**	0.6	0.250	1000	1.11	14.3	3.33	130.8
3	**1**	0.8	0.323	1292	2.02	12.3	3.52	130.2
4	**1**	1.0	0.350	1400	3.75	10.4	3.22	129.4
5	**1**	1.2	0.532	2128	5.12	7.97	3.43	125.5
6	**2**	0.4	0.194	776	trace	14.7	2.94	135.6
7	**2**	0.8	0.239	956	040	12.8	2.53	133.2
8	**2**	1.2	0.265	1060	0.84	10.5	2.60	129.5
9	**3**	0.4	0.186	744	trace	18.2	2.20	134.3
10	**3**	0.8	0.332	1328	0.46	15.6	2.87	131.2
11	**3**	1.2	0.500	2000	0.90	13.7	3.14	130.2
12	**4**	0.8	trace	—	—	—	—	—

[a] Polymerization conditions: toluene + 1-hexene total 70 mL, catalyst 1 ×10^{-6} mol, Al : Zr molar ratio 300, B : Zr molar ratio 1.5, time 15 min, temperature 60 °C, ethylene pressure 5 bar. [b] Activity in g polymer (mmol Zr)$^{-1}$ h^{-1}. [c] Calculated based on ^{13}C NMR spectra. [d] Determined by GPC in *o*-dichlorobenzene *vs.* polystyrene standard. [e] Determined by DSC at a heating rate of 10 °C min^{-1}; the data from the second scan are used.

order of **1** > **3** > **2** > **4**. The **4**–Al^{i}Bu$_3$–Ph$_3$CB(C$_6$F$_5$)$_4$ catalyst system shows very low catalytic activity for the copolymerization reaction and only a trace amount of polymer was obtained. As discussed above for the ethylene homopolymerization, the low catalytic activity of the **4**–Al^{i}Bu$_3$–Ph$_3$CB(C$_6$F$_5$)$_4$ catalyst system may be caused mainly by the difficult activation process of complex **4**. The catalytic activity of complexes **1–3** for the copolymerization reaction was found to increase with an increase of the feed concentration of 1-hexene from 0.40 mol L^{-1} to 1.20 mol L^{-1}. A similar comonomer effect has previously been observed in the ethylene–1-hexene copolymerization with other zirconium catalyst systems.[32,33]

The ethylene–1-hexene copolymers were analyzed by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of a typical copolymer sample is shown in Fig. 4. No resonance ranging from 40–42 ppm for the α,α-carbon in the HH dyad sequence[34] was observed in the ^{13}C NMR spectra, indicating that 1-hexene units are essentially isolated by ethylene units in the polymer chains. The comonomer content of the ethylene–1-hexene copolymers were calculated based on ^{13}C NMR analysis,[34] and the results are given in Table 3. 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 complex **1** are obviously higher than those of the copolymers produced by complexes **2** and **3** under similar conditions. The comonomer incorporation ability of a catalyst system can be affected by several factors.[35] In the present work, the steric bulk of the anilide ligand seems to be a major factor. An adequate steric hindrance from the ligands would weaken the interaction between the cationic catalyst and the anionic cocatalyst species, which would favor coordination of the comonomer to the metal center of the catalyst. However, an excessively bulky coordination environment would block the coordination of the comonomer.[36] GPC analysis reveals that the obtained ethylene–1-hexene copolymers possess relatively high molecular weight values ($Mw = 8–16 \times 10^4$ g mol^{-1}). The molecular weight distribution (MWD) of the copolymers is relatively narrow, which is characteristic of LLDPE produced using a metallocene catalyst.[37] The molecular weight values of the obtained copolymers are dependent on the structure of the catalyst and the comonomer content. In addition, DSC analysis indicates that the melting temperatures of the resultant copolymers decrease with an increase in the comonomer content, which is similar to the previous observations for ethylene–α-olefin copolymers with other single site catalyst systems.[38]

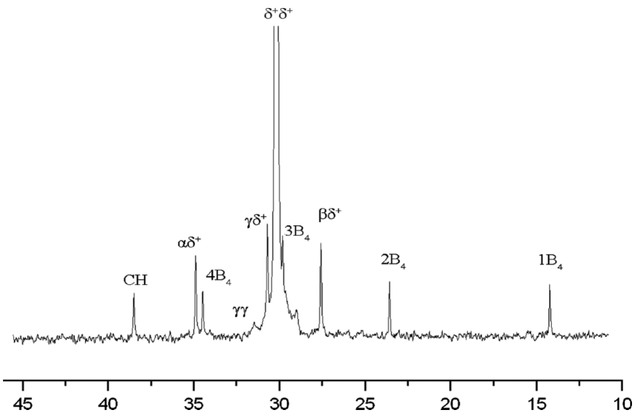
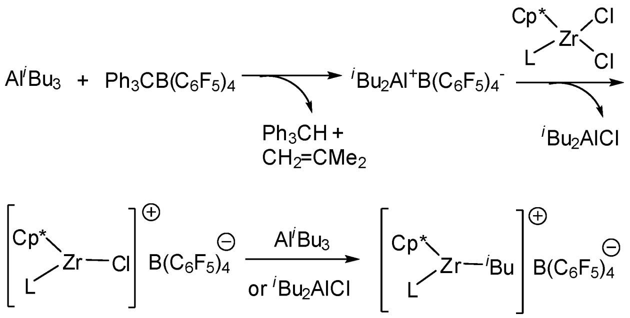


Fig. 4 ^{13}C NMR spectrum for poly(ethylene-*co*-1-hexene) obtained with **1**–Al^{i}Bu$_3$–Ph$_3$CB(C$_6$F$_5$)$_4$ (run 5 in Table 3).

Studies on catalyst activation procedure

To understand the activation procedure of these catalyst systems, reactions of complexes **2** and **4** with Al^{i}Bu$_3$ and Ph$_3$CB(C$_6$F$_5$)$_4$ were studied by ^{1}H NMR spectroscopy, and the results are shown in Fig. S1 and S2 in the supporting information.† When complex **2** was treated with about 5 equiv of Al^{i}Bu$_3$ in C$_7$D$_8$, almost only signals for complex **2** and Al^{i}Bu$_3$ can be observed (see A–C in Fig. S1†) even after the reaction mixture was heated to 60 °C for an hour, indicating that no reaction has taken place. However, upon addition of Ph$_3$CB(C$_6$F$_5$)$_4$ to the mixture of **2** and Al^{i}Bu$_3$, reactions take place immediately with the formation of Ph$_3$CH (singlet, 5.37 ppm) and CH$_2$═CMe$_2$ (septet, 4.71 ppm and triplet, 1.60 ppm) as seen in Fig. S1D.† Similar results were obtained from the reaction of **4** with Al^{i}Bu$_3$ and Ph$_3$CB(C$_6$F$_5$)$_4$ except that this reaction is relatively slow, as shown in Fig. S2.† The formation of Ph$_3$CH and CH$_2$═CMe$_2$ was also observed from the reaction of

Al^iBu_3 and $Ph_3CB(C_6F_5)_4$ as reported previously.[39] These observations imply that the activation of these catalyst systems begins with the abstraction of a β-H of the Al^iBu_3 by the Ph_3C^+ cation to form a $^iBu_2Al^+$ cation, Ph_3CH and $CH_2{=}CMe_2$ as shown in Scheme 2. The $^iBu_2Al^+$ cation can react either with Al^iBu_3 to form $^iBu_2AlH$, $CH_2{=}CMe_2$ and a new $^iBu_2Al^+$ cation, or with the precatalyst to produce $Cp^*ZrCl[N(2,6\text{-}R^1{}_2C_6H_3)R^2]^+$ and $^iBu_2AlCl$. The produced $Cp^*ZrCl[N(2,6\text{-}R^1{}_2C_6H_3)R^2]^+$ further reacts with Al^iBu_3, $^iBu_2AlH$ or $^iBu_2AlCl$ to form the final catalytically active species $Cp^*Zr^iBu[N(2,6\text{-}R^1{}_2C_6H_3)R^2]^+$ or $Cp^*ZrH[N(2,6\text{-}R^1{}_2C_6H_3)R^2]^+$. The ^1H NMR spectra of the **2**–Al^iBu_3–$Ph_3CB(C_6F_5)_4$ and **4**–Al^iBu_3–$Ph_3CB(C_6F_5)_4$ mixtures show some broad signals, which seems to demonstrate that the formed catalytically active species of half-sandwich zirconium in these systems are either unstable or exist in different forms by combining with Al^iBu_3, $^iBu_2AlH$, $^iBu_2AlCl$, $^iBuAlCl_2$ and $B(C_6F_5)_4^-$. Similar results have been reported in literature.[39]



Scheme 2 A possible mechanism for the catalyst activation procedure.

Conclusions

A number of half-zirconocene anilide complexes of the type $Cp^*ZrCl_2[N(2,6\text{-}R^1{}_2C_6H_3)R^2]$ and $Cp^*ZrCl[N(2,6\text{-}Me_2C_6H_3)Me]_2$ have been synthesized in good yields from the reactions of Cp^*ZrCl_3 with the corresponding lithium anilide. These new zirconium complexes were all characterized by ^1H and ^{13}C NMR spectroscopy, as well as elemental analysis. Single crystal X-ray diffraction analysis on complexes **1**, **2** and **4** reveals that these complexes have a pseudo-octahedral coordination environment in their solid state and adopt a three-legged piano stool geometry with the anilide N and Cl atoms being the three legs and the Cp* ring being the seat. Upon activation with Al^iBu_3–$Ph_3CB(C_6F_5)_4$, complexes **1–4** exhibit good catalytic activity for ethylene polymerization, producing moderate molecular weight polyethylene. Complexes **1–3** also show good catalytic activity for ethylene–1-hexene copolymerization in the presence of Al^iBu_3–$Ph_3CB(C_6F_5)_4$, producing poly(ethylene-*co*-1-hexene)s with relatively high molecular weight. The catalytic activity of complexes **1–4** for both ethylene polymerization and ethylene–1-hexene copolymerization changes in the order of **1** > **3** > **2** > **4**. The comonomer incorporation ability of complexes **1–3** under similar conditions decreases in the order of **1** > **3** > **2**. ^1H NMR studies on the reactions of complexes **2** and **4** with Al^iBu_3 and $Ph_3CB(C_6F_5)_4$ indicate that these zirconium complexes do not react directly with Al^iBu_3 in the absence of $Ph_3CB(C_6F_5)_4$.

Experimental

General comments

All manipulations involving air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere (ultra-high purity) using either standard Schlenk techniques or glove box techniques. Toluene, diethyl ether, and *n*-hexane were distilled under nitrogen in the presence of sodium and benzophenone. 1-Hexene were purified by distilling over calcium hydride before use. Cp^*ZrCl_3,[40] $HN(2,6\text{-}R^1{}_2C_6H_3)R^2$ [$R^1 = {}^iPr$, $R^2 = Me$ (**HLa**); $R^1 = Me$, $R^2 = Me$ (**HLb**); $R^1 = {}^iPr$, $R^2 = Bn$ (**HLc**)][25] and $Ph_3CB(C_6F_5)_4$[41] were prepared according to literature procedures. Polymerization grade ethylene was further purified by passage through columns of 5 Å molecular sieves and MnO. Al^iBu_3, *n*-BuLi, and $ZrCl_4$ were purchased from Aldrich or Acros. ^1H and ^{13}C NMR spectra were measured using a Varian Mercury-300 NMR spectrometer. ^{13}C NMR spectra of the copolymers were recorded on a Varian Unity-400 NMR spectrometer at 125 °C with $o\text{-}C_6D_4Cl_2$ as the solvent. The 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 polymer 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 $LiN(2,6\text{-}R^1{}_2C_6H_3)R^2$. The lithium salts of the anilide ligands, $LiN(2,6\text{-}R^1{}_2C_6H_3)R^2$, were prepared according to the following typical procedure. A solution of *n*-BuLi (1.60 M in *n*-hexane, 14.2 mL, 22.7 mmol) was slowly added to a solution of $HN(2,6\text{-}{}^iPr_2C_6H_3)Me$ (4.34 g, 22.7 mmol) in *n*-hexane (15 mL) at −20 °C. A large amount of white precipitate formed during the addition. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. The resultant precipitate was collected on a frit, washed with cold *n*-hexane (2 × 10 mL) and dried under vacuum to give the pure product (3.09 g, 15.7 mmol, 69%).

Synthesis of $Cp^*ZrCl_2[N(2,6\text{-}{}^iPr_2C_6H_3)CH_3]$ (1). $LiN(2,6\text{-}{}^iPr_2C_6H_3)CH_3$ (0.540 g, 2.74 mmol) was added to a suspension of Cp^*ZrCl_3 (0.910 g, 2.74 mmol) in 40 mL diethyl ether at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure, and the residue was extracted with 50 mL of hexane. After filtration, the filtrate was concentrated to 15 mL and stored at −25 °C several days. Pure **1** was obtained as colorless crystals (0.865 g, 1.78 mmol, 65%) (Found: C, 57.1; H, 7.20; N 2.83. $C_{23}H_{35}Cl_2NZr$ requires C, 56.7; H, 7.23; N, 2.87%). Mp: 252–254 °C. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ 7.06–7.22 (m, 3H, Ar*H*), 3.50 (s, 3H, NCH_3), 3.00 (sept, 2H, $CHMe_2$, $^3J_{H\text{–}H} = 6.9$ Hz), 1.98 (s, 15H, Cp*Me*$_5$), 1.33 (d, 6H, $CHMe_2$, $^3J_{H\text{–}H} = 6.9$ Hz), 1.14 (d, 6H, $CHMe_2$, $^3J_{H\text{–}H} = 6.9$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ 144.3, 126.1, 125.0, 123.8, 122.1, 38.7, 27.2, 27.0, 23.9, 11.8.

Synthesis of $Cp^*ZrCl_2[N(2,6\text{-}Me_2C_6H_3)CH_3]$ (2). Complex **2** was synthesized using a procedure identical to that for complex **1** with $LiN(2,6\text{-}Me_2C_6H_3)CH_3$ (0.424 g, 3.00 mmol) and Cp^*ZrCl_3 (1.00 g, 3.00 mmol) as starting materials. Pure **2** was obtained as colorless crystals (0.921 g, 2.13 mmol, 71%) (Found: C, 52.6; H, 6.38; N, 3.23. $C_{19}H_{27}Cl_2NZr$ requires C, 52.9; H, 6.31; N, 3.25%).

Table 4 Crystallographic parameters, data collections, and structure refinements for complexes **1**, **2** and **4**

Complexes	**1**	**2**	**4**
Formula	$C_{23}H_{35}Cl_2NZr$	$C_{19}H_{27}Cl_2NZr$	$C_{28}H_{39}ClN_2Zr$
Fw	487.64	431.54	530.28
Wavelength (A)	0.71073	0.71073	0.71073 A
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	P2(1)2(1)2(1)	P2(1)/n	P-1
a (Å)	9.2297(3)	8.189(5)	8.4521(8)
b (Å)	12.1798(4)	27.869(19)	11.6652(11)
c (Å)	21.4452(8)	9.933(7)	14.8715(14)
α (deg)	90	90	85.017(2)
β (deg)	90	114.34	75.515(2)
γ (deg)	90	90	73.171(2)
V (Å^3)	2410.78(14)	2066(2)	1358.7(2)
Z	4	4	2
F(000)	1016	888	556
D_c (g cm^{-3})	1.344	1.388	1.296
Abs. coeff. (mm^{-1})	0.686	0.790	0.520
Crystal size (mm)	0.23 × 0.16 × 0.12	0.23 × 0.18 × 0.15	0.21 × 0.17 × 0.12
θ range (deg)	1.90–26.02	1.46–26.61	1.41–25.04
No. of reflns	13134	12197	6859
No. of indep. reflns	4729	4169	4699
R(int)	0.0168	0.0497	0.0391
Data/restraints/parameters	4729/0/254	4169/90/302	4699/0/300
GOF	1.048	1.029	0.977
$R1$, Rw [$I > 2\sigma(I)$]	0.0208, 0.0525	0.0438, 0.0989	0.0523, 0.1055
$R1$, Rw (all data)	0.0217, 0.0530	0.0701, 0.1079	0.0820, 0.1183
Max(min) diff. peak (e Å^{-3})	0.293, –0.245	0.472, –0.364	0.548, –0.469

Mp: 129–132 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 6.97–7.12 (m, 3H, Ar*H*), 3.41 (s, 3H, NC*H*$_3$), 2.13 (s, 6H, ArC*H*$_3$), 1.92 (s,15H, Cp*Me*$_5$). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ 133.2, 128.3 125.3, 124.8, 124.3. 36.0, 17.5, 11.4.

Synthesis of Cp*ZrCl$_2$[N(2,6-^{i}Pr$_2$C$_6$H$_3$)Bn] (3). Compound **3** was synthesized using a procedure identical to that for **1** with Cp*ZrCl$_3$ (1.00 g, 3.00 mmol) and LiN(2,6-^{i}Pr$_2$C$_6$H$_3$)Bn (0.821 g, 3.00 mmol) as starting materials. Pure **3** was obtained as colorless crystals (1.35 g, 2.39 mmol, 80%) (Found: C, 61.6; H, 6.98; N, 2.46. $C_{29}H_{39}Cl_2NZr$ requires C, 61.8; H, 6.97; N, 2.48%). Mp: 222–225 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 6.94–7.22 (m, 8H, Ar*H*), 4.85 (s, 2H, NC*H*$_2$), 2.98 (sept, 2H, C*H*Me$_2$, $^3J_{H-H}$ = 6.6 Hz), 2.10 (s, 15H, Cp*Me*$_5$), 1.22 (d, 6H, CH*Me*$_2$, $^3J_{H-H}$ = 6.6 Hz), 0.59 (d, 6H, CH*Me*$_2$, $^3J_{H-H}$ = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ 145.4, 137.7, 130.4, 128.1, 127.6, 126.3, 125.5, 124.1, 54.3, 27.4, 25.9, 25.0, 12.1.

Synthesis of Cp*ZrCl[N(2,6-Me$_2$C$_6$H$_3$)CH$_3$]$_2$ (4). Complex **4** was synthesized using a procedure identical to that for complex **1** with LiN(2,6-Me$_2$C$_6$H$_3$)CH$_3$ (0.423 g, 3.00 mmol) and Cp*ZrCl$_3$ (0.500 g, 1.50 mmol) as starting materials. Pure **3** was obtained as colorless crystals (0.599 g, 1.13 mmol, 75%) (Found: C, 63.6; H, 7.48; N, 5.26. $C_{28}H_{39}ClN_2Zr$ requires C, 63.4; H, 7.41; N, 5.28%). Mp: 120–123 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ 6.99 (d, 4H, Ar*H*, $^3J_{H-H}$ = 7.5 Hz), 6.87 (t, 2H, Ar*H*, $^3J_{H-H}$ = 7.5 Hz), 2.85 (s, 6H, NC*H*$_3$), 2.17 (s, 12H, ArC*H*$_3$), 1.91 (s, 15H, Cp*Me*$_5$). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ 151.9, 128.3, 128.1, 124.2, 121.9, 37.6, 31.2, 11.2.

X-Ray structural analysis of complexes 1, 2 and 4

All measurements were made on a Rigaku RAXIS-RAPID diffractometer with Mo-Kα (λ = 0.71073 Å) radiation. The structures were solved by direct method[42] and refined by full-matrix least-squares on F^2. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in idealized position. All calculations were performed using the SHELXTL crystallographic software packages.[43] Details of the crystallographic parameters, data collections, and structure refinements are summarized in Table 4.

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 the desired temperature and saturated with ethylene (1.0 atm). The polymerization reaction was started by addition of a mixture of the catalyst and Al^{i}Bu$_3$ in toluene (5 mL) and a solution of $Ph_3CB(C_6F_5)_4$ in toluene (5 mL) at the same time. The vessel was pressurized to 5 atm with ethylene immediately and the pressure was maintained 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 ethanol containing HCl (3 M). The polymer was collected by filtration, washed with water and ethanol, and dried to a constant weight under vacuum. For the ethylene–1-hexene copolymerization experiments, appropriate amounts of 1-hexene were added in toluene.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 21074043 and 20772044).

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