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Ethylene polymerization with long-lifetime monopendant thienyl-substituted group 4 metallocenes

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A series of group 4 metallocenes (RCp)[Cp—(bridge)—(2-C_4H_3S)]MCl_2 [M = Ti (C1–C4); M = Zr (C5–C8)] bearing a pendant thiophene group on a cyclopentadienyl ring have been synthesized, characterized and tested as catalyst precursors for ethylene polymerization. The molecular structures of representative titanocenes C2 and C4 were confirmed by single-crystal X-ray diffraction and revealed that both complexes exist in an expected coordination environment for a monomeric bent metallocene. No intramolecular coordination between the thiophene group and the titanium center could be observed in the solid state. Upon activation by methylaluminoxane (MAO), titanocenes C1–C4 showed moderate catalytic activities and produced high- or ultra-high-molecular-weight polyethylene (M_v 70.5–227.1 × 10^4 g mol^{-1}). Titanocene C3 is more active and long-lived, with a lifetime of nearly 9 h at 30 °C. At elevated temperatures of 80–110 °C, zirconocenes C5–C8 displayed high catalytic activities (up to 27.6 × 10^5 g PE (mol Zr)$^{-1}$ h^{-1}), giving high-molecular-weight polyethylene (M_v 11.2–53.7 × 10^4 g mol^{-1}). Even at 80 °C, a long lifetime of at least 2 h was observed for the C8/MAO catalyst system. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: titanocene; zirconocene; thiophene; polymerization; ethylene

Introduction

Over the past decades, a significant amount of research has been directed toward the development of group 4 metallocene catalysts owing to their high catalytic activities for olefin polymerization and fine control over polymer microstructures.[1–3] We noticed that modification of the steric and electronic properties at the metal center by varying the ligand structure has a strong influence on the catalytic behavior. One of the great achievements in metallocene catalyst design is the constrained geometry complexes (namely CGC catalysts), which contain a sidearm bearing an additional chelating donor functionality at the cyclopentadienyl (Cp) ring and show excellent activity for copolymerization of ethylene and α-olefins to give novel copolymers.[4–11]

Recently, many examples of half-sandwich metallocenes bearing soft pendant donors such as S-donor, P-donor, alkyl and aryl groups on the Cp ring have been reported.[12–18] In 2001, Hessen *et al.* developed a series of half-sandwich titanocenes with an arene-pendant Cp ligand,[12] which are excellent catalysts for ethylene trimerization after activation with methylaluminoxane (MAO). The authors proposed that this remarkable behavior may be attributed to the arene-pendant moiety, which is likely to exhibit hemilabile behavior by η^6 coordination.[12,13] In our previous work, we reported that half-sandwich titanocenes with a thiophene-pendant Cp ligand[14] could selectively trimerize ethylene to 1-hexene with high activity. It could be envisaged that the heterocycle thiophene as an aromatic system may coordinate to the metal center in the η^5 mode, and also the heteroatom as a donor may coordinate to the metal center in the η^1 mode. The thiophene—Cp ligand may serve as a hemilabile ligand in the catalytic trimerization of ethylene. However, to date only a few examples of group 4 metallocene catalysts bearing sidearm donors on the Cp rings have been reported for olefin polymerization.[19–21]

To further understand the effects of the extra donor on the Cp ring as well as the relationship between catalyst structures and their catalytic behavior, herein we report the syntheses and characterization of a series of monopendant thienyl-substituted group 4 metallocenes, and explore the effect of the pendant thiophene group toward the catalytic behavior for ethylene polymerization in the presence of MAO.

Results and Discussion

Synthesis of Group 4 Metallocenes (RCp)[Cp—(bridge)—(2-C_4H_3S)]MCl_2 (C1–C8)

The desired group 4 metallocenes (RCp)[Cp—(bridge)—(2-C_4H_3S)]MCl_2 [M = Ti (**C1–C4**); M = Zr (**C5–C8**)] bearing a pendant thiophene group on a Cp ring were synthesized in moderate to good yields (35.1–70.6%) by the reaction of (R^3Cp)$TiCl_3$ or (R^3Cp)$ZrCl_3$·DME with 1 equiv. of lithium salts [Cp—(bridge)—(2-C_4H_3S)]Li that were prepared *in situ* by treating the corresponding substituted fulvenes with 2-thienyl lithium (Scheme 1). The resultant group 4 metallocenes **C1–C8** were characterized by ^{1}H and ^{13}C NMR and elemental analysis.

In the ^{1}H NMR spectra of **C1–C8**, the chemical shift of the proton *ortho* to the thiophene group appeared at δ = 7.16–7.30 ppm,

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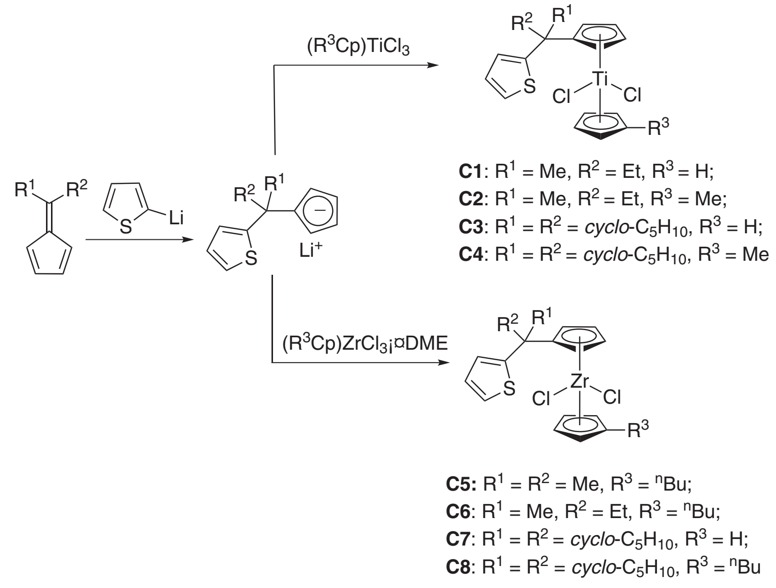


Scheme 1. Synthesis of titanocenes **C1–C4** and zirconocenes **C5–C8**.

which is similar to that observed for half-sandwich titanium complex [Cp-C(*cyclo*-C_5H_{10})-(2-C_4H_3S)]$TiCl_3$ (at 7.25 ppm).[14] These results indicate no obvious coordination between the thiophene group and the metal center in these metallocenes **C1–C8** in solution.

Crystal Structures of Titanocenes C2 and C4

Single crystals of titanocenes **C2** and **C4** suitable for X-ray diffraction studies were obtained from dichloromethane/^{n}hexane solution at room temperature. The molecular structures of **C2** and **C4** are shown in Figs 1 and 2, respectively. The crystallographic data and structure refinement details are summarized in Table 1, and the selected bond lengths and angles are listed in Table S1 (supporting information).

Both **C2** and **C4** were found to be an expected monomeric bent metallocene compound. As shown in Fig. 1, for example, the Ti—C bond lengths of both the alkyl-substituted Cp ring and the thienyl-substituted Cp ring in **C2** vary between 2.322(2) and 2.467(2) Å in accordance with an η^5 coordination of the two Cp ligands to the metal center. The Ti—C distances to the substituted carbon are generally longer than that to the unsubstituted carbon in the Cp ring. The average Ti—Cl bond lengths of approximately 2.36 Å is comparable to those previously reported for titanocenes.[22,23] The Cl1—Ti1—Cl2 bond angle is 93.40(3)°, indicating that the two chlorides are located in a *cis* position to each other. It should be noted that the Ti1—S1 distance is 4.33 Å, indicating no intramolecular coordination between the thiophene group as a pendant donor and the titanium center in the solid state.

Ethylene Polymerization Catalyzed by Titanocenes C1–C4

The catalytic behavior of titanocenes **C1–C4** for ethylene polymerization were evaluated using MAO as cocatalyst. The polymerization results are summarized in Table 2. Under the same conditions, titanocenes **C1–C4** exhibited similar activities but gave much higher molecular-weight polyethylene (M_v 112.8–155.7 × 10^4 g mol^{-1}) in comparison to that obtained by Cp_2TiCl_2 (M_v 52.6 × 10^4 g mol^{-1}) (Fig. 3 and Table 2, entries 1, 4–7).

The structures of these titanocenes have an important influence on the catalytic activity. The activity increases with the increase in the steric hindrance of the bridging unit at R^1 and R^2 in the thienyl-substituted Cp moiety. For example, under the same conditions, **C4** with a cyclohexyl bridge ($R^1 = R^2 =$ *cyclo*-C_5H_{10}) displayed much higher catalytic activity (1.9 × 10^5 g PE (mol Ti)$^{-1}$ h^{-1}) than **C2**, which features a smaller CMeEt bridge (R^1 = Me, R^2 = Et) (1.0 × 10^5 g PE (mol Ti)$^{-1}$ h^{-1}) (entry 7 vs. entry 5). Although no coordination between the thiophene group and the titanium center could be observed in the solid state of titanocenes **C2** and **C4**, the thiophene group could coordinate to the generated low-valence titanium species when these titanocenes were activated by MAO.[14] We postulate that the introduction of more bulky substituents on the bridge unit might be beneficial to push the pendant thiophene group toward the

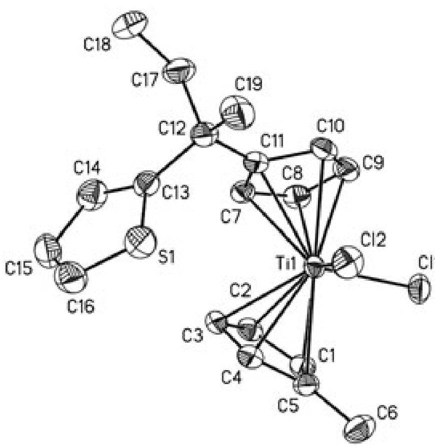


Figure 1. Molecular structure of titanocene **C2**, with displacement ellipsoids at the 50% probability level; hydrogen atoms are omitted for clarity.

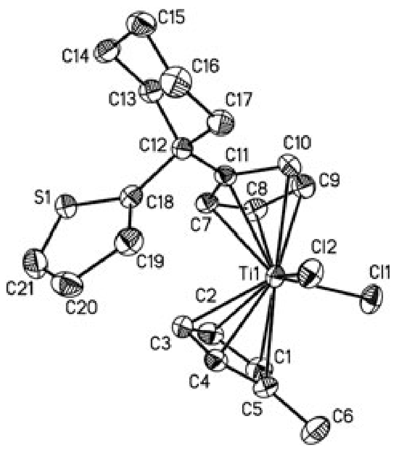


Figure 2. Molecular structure of titanocene **C4**, with displacement ellipsoids at the 50% probability level; hydrogen atoms are omitted for clarity.

Table 1. Crystal data and structure refinement for titanocenes **C2** and **C4**

	C2	**C4**
Empirical formula	$C_{19}H_{22}Cl_2STi$	$C_{21}H_{24}Cl_2STi$
Formula weight	401.23	427.26
Space group	$P2_1/c$	$P2_1/c$
Crystal system	Monoclinic	Monoclinic
a (Å)	8.2850(7)	8.6899(13)
b (Å)	17.7467(15)	18.048(3)
c, Å	12.9976(11)	13.0417(19)
β (°)	105.043(2)	107.878(3)
V (Å^3)	1845.6(3)	1946.6(5)
Z	4	4
D_{calcd} (Mg m^{-3})	1.444	1.458
Absorption coefficient (mm^{-1})	0.863	0.823
$F(000)$	832	888
Crystal size (mm)	0.11 × 0.13 × 0.21	0.11 × 0.15 × 0.21
θ range (°)	2.0–26.0	2.3–26.0
Reflections collected/unique	11058/3620 [R_{int} = 0.027]	11743/3833 [R_{int} = 0.079]
Data with $I > 2\sigma(I)$ / restraints / parameters	3027 / 7 / 238	2264 / 12 / 245
Goodness–of–fit on F^2	1.04	0.95
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.038, wR_2 = 0.096	R_1 = 0.049, wR_2 = 0.089
R indices (all data)	R_1 = 0.048, wR_2 = 0.102	R_1 = 0.102, wR_2 = 0.107
Largest diff. peak and hole (e Å^{-3})	0.38 and −0.19	0.34 and −0.29

titanium center[15] and strengthen the intramolecular coordination interaction, thus improving the stability of the catalytically active species and leading to higher activity. Similar results were also observed for analogues **C1** and **C3** (entry 4 vs. entry 6). **C3** with a cyclohexyl bridge also displayed relatively higher catalytic activity (3.2 × 10^5 g PE (mol Ti)$^{-1}$ h^{-1}) than **C1** with a smaller CMeEt bridge (1.8 × 10^5 g PE (mol Ti)$^{-1}$ h^{-1}).

The R^3 groups on the alkyl-substituted Cp moiety also play an important role on the catalytic activity. **C2** with Me group at the R^3 position displayed relatively lower catalytic activity than **C1** (R^3 = H) (entry 5 vs. entry 4). A similar trend was also observed for analogs **C3** (R^3 = H) and **C4** (R^3 = Me) (entry 6 vs. entry 7). These data suggest that the decrease in the steric bulk of the groups at R^3 position is beneficial to the catalytic activity.

The influences of Al/Ti molar ratio, reaction temperature and ethylene pressure were studied by titanocene **C3** as pre-catalyst. With the increase of the Al/Ti molar ratio from 1000 to 9000, the catalytic activity was increased from 1.7 × 10^5 to 3.9 × 10^5 g PE (mol Ti)$^{-1}$ h^{-1} (entries 6, 8–11). Meanwhile, the M_v value of the resultant polyethylene was significantly decreased from 190.3 × 10^4 to 70.5 × 10^4 g mol^{-1}, which is possibly due to the enhanced rate of chain transfer to aluminum for the termination.[24] Upon increasing the ethylene pressure, both the catalytic activity and the molecular weight increased consistently (entries 6, 12–14). The temperature rise led to enhancement first and then decrease in the catalytic activity (entries 6, 15–18). Although the highest activity of 3.2 × 10^5 g PE (mol Ti)$^{-1}$ h^{-1} was obtained at 30 °C, moderate activity of 1.5 × 10^5 g PE (mol Ti)$^{-1}$ h^{-1} was still maintained at elevated temperature up to 80 °C (entry 17). In addition, the M_v value of the resultant polyethylene significantly decreased upon increase in temperature. This can be attributed to a facilitated chain transfer reaction via β-H elimination at elevated temperatures.[25]

It is worth noting that the most active pre-catalyst, **C3**, is remarkably long-lived at ambient temperature. The yield of the obtained polyethylene was continuously increased during the polymerization time from 30 min to 9 h (Fig. 4, entries 6, 19–22). Although the catalytic activity decreases with prolonged polymerization time, **C3** still retains moderate activity of 0.9 × 10^5 g PE (mol Ti)$^{-1}$ h^{-1} in 9 h. By contrast, for pre-catalyst Cp_2TiCl_2, no obvious increase in polyethylene yield was observed after 1 h, indicating a short-lived pro-catalyst for ethylene polymerization. A half-sandwich titanium complex bearing a pendant thiophene group was previously reported by Huang *et al.*[14] The authors proposed that the thiophene group could coordinate to the generated low-valence titanium center when the half-sandwich catalyst is activated by MAO. By analogy, when activated by MAO, the remarkably long catalytic lifetime (nearly 9 h) of titanocene **C3** may be attributable to the coordination ability of the thiophene group, which can stabilize the generated active catalytic species, thus leading to the formation of high- or ultra-high-molecular-weight polyethylene (up to 227.1 × 10^4 g mol^{-1}).

Ethylene Polymerization Catalyzed by Zirconocenes C5–C8

Upon activation with MAO, zirconocenes **C5–C8** were investigated as the catalysts for ethylene polymerization in detail (Table 3). As observed for titanocenes **C1**–**C4**, a similar trend was observed for zirconocenes **C5**–**C8**, which feature a pendant thiophene group on a Cp ring that proved beneficial to the production of relatively higher molecular weight polyethylene in comparison with the typical Cp_2ZrCl_2 catalyst (Fig. 5).

Similar to that observed for titanocenes **C1–C4**, for zirconocenes **C5–C8** the catalytic activity increased remarkably by increasing the steric hindrance of the bridging unit at R^1 and R^2 in the thienyl-substituted Cp moiety. For example, at 80 °C, **C8** with a cyclohexyl as the bridging unit was more beneficial to the catalytic activity (15.4 × 10^5 g PE (mol Zr)$^{-1}$ h^{-1}) than **C6**, which has a relatively smaller bridge CMeEt (9.6 × 10^5 g PE (mol Zr)$^{-1}$ h^{-1}) (entry 34 vs. entry 28). **C5**, with the smallest bridge group CMe_2, showed the lowest catalytic activity (3.2 × 10^5 g PE (mol Zr)$^{-1}$ h^{-1}) for ethylene polymerization under the same conditions (entry 26). This result indicates that the catalytic activity followed the order **C8** (R^1 = R^2 = *cyclo*-(C_5H_{10}) > **C6** (R^1 = Me, R^2 = Et) > **C5** (R^1 = R^2 = Me).

When compared with **C8**, which has a sterically larger ^{n}Bu group at the R^3 position on the alkyl-substituted Cp moiety, **C7** (R^3 = H) displayed much lower catalytic activity (3.3 × 10^5 g PE (mol Zr)$^{-1}$ h^{-1}) (entry 30). By contrast, titanocenes **C4**, with a relatively bulky Me group at R^3, showed relatively lower activity than **C3** (R^3 = H). Rytter and co-workers reported a series of zirconocenes $(RCp)_2ZrCl_2$ with linear alkyl substituents on ethylene polymerization and found that the zirconocene with ^{n}Bu substituent showed increased activity compared to Cp_2ZrCl_2.[26] It was proposed that the higher activity resulted from an agostic interaction between the metal center and a hydrogen on the linear alkyl substituent having at least three carbon atoms.[26,27] So it is possible that the increased activity in **C8** compared to **C7** (R = H) may also be attributed to the agostic interaction between the Zr and a γ-H on the ^{n}Bu substituent in **C8**.

Table 2. Ethylene polymerization results catalyzed by titanocenes **C1–C4**/MAO catalytic systems[a]

Entry	Catalyst	Al/Ti	Temp (°C)	Time (min)	Pressure (MPa)	Yield (mg)	Activity[b]	M_V[c] (10^4 g mol^{-1})
1	Cp_2TiCl_2	3000	30	30	0.6	137	2.7	52.6
2	Cp_2TiCl_2	3000	30	1 h	0.6	167	1.7	54.3
3	Cp_2TiCl_2	3000	30	3 h	0.6	172	0.6	55.1
4	**C1**	3000	30	30	0.6	92	1.8	128.7
5	**C2**	3000	30	30	0.6	51	1.0	112.8
6	**C3**	3000	30	30	0.6	160	3.2	144.1
7	**C4**	3000	30	30	0.6	95	1.9	155.7
8	**C3**	1000	30	30	0.6	84	1.7	190.3
9	**C3**	2000	30	30	0.6	127	2.5	163.5
10	**C3**	6000	30	30	0.6	183	3.7	116.9
11	**C3**	9000	30	30	0.6	194	3.9	70.5
12	**C3**	3000	30	30	0.1	61	1.2	77.2
13	**C3**	3000	30	30	0.3	103	2.1	95.3
14	**C3**	3000	30	30	1.0	204	4.1	158.3
15	**C3**	3000	0	30	0.6	94	1.9	185.2[d]
16	**C3**	3000	50	30	0.6	91	1.8	107.5
17	**C3**	3000	80	30	0.6	75	1.5	74.1[d]
18	**C3**	3000	110	30	0.6	Trace	—	—
19	**C3**	3000	30	1 h	0.6	276	2.8	172.3
20	**C3**	3000	30	3 h	0.6	433	1.4	202.1
21	**C3**	3000	30	6 h	0.6	715	1.2	227.1
22	**C3**	3000	30	9 h	0.6	776	0.9	225.7

[a] Polymerization conditions: 1 μmol of catalyst, solvent toluene (total volume 25 ml).
[b] Activity in 10^5 g PE (mol Ti)$^{-1}$ h^{-1}.
[c] Intrinsic viscosity was determined in decahydronaphthalene at 135 °C and molecular weight was calculated using the relation $[\eta] = 6.77 \times 10^{-4} M_V^{0.67}$.
[d] M_w and M_w/M_n were determined by GPC. For entry 15, $M_w = 189.5 \times 10^4$ g mol^{-1}, $M_w/M_n = 2.32$. For entry 17, $M_w = 73.6 \times 10^4$ g mol^{-1}, $M_w/M_n = 2.10$.

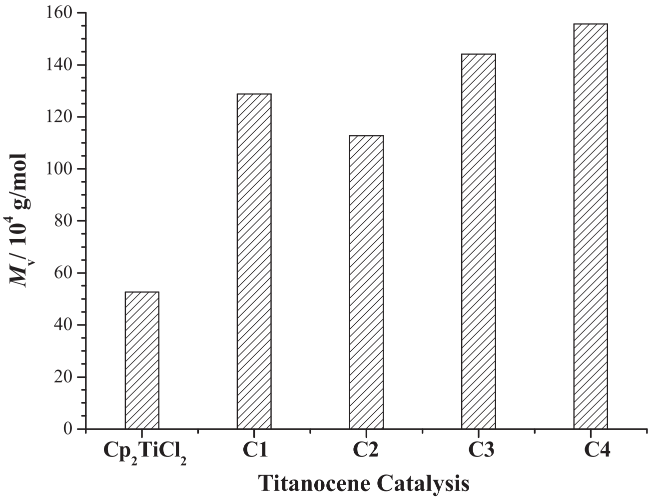


Figure 3. Viscosity average molecular weight (M_v) of polyethylene obtained by titanocenes Cp_2TiCl_2/MAO and **C1–C4**/MAO at 30 °C in 30 min (Table 2, entries 1, 4–7).

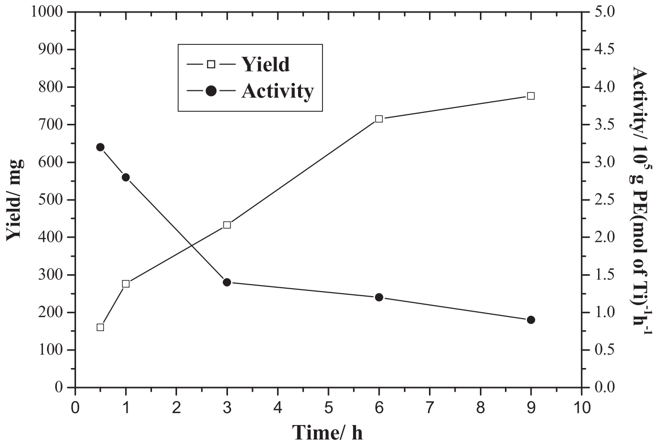


Figure 4. Plots of polymerization time versus catalytic activity (●) and polymer yield (□) of the polyethylene obtained by **C3**/MAO at 30 °C (Table 2, entries 6, 19–22).

The performance of pre-catalyst **C8** was investigated in detail by changing the reaction parameters such as Al/Zr molar ratio, polymerization temperature and ethylene pressure (entries 32–43). The catalytic activity significantly increased from 0.5 × 10^5 g PE (mol Zr)$^{-1}$ h^{-1} at 30 °C to 21.9 × 10^5 g PE (mol Zr)$^{-1}$ h^{-1} at 110 °C (entries 32–35). Meanwhile, the M_v value of the resultant polyethylene significantly decreased from 58.2 × 10^4 to 13.1 × 10^4 g mol^{-1} as reaction temperature increased due to a faster chain transfer reaction via β-H elimination at higher temperature.

The variation of the Al/Zr molar ratio had a significant influence on the catalytic activity and the molecular weight of the resultant polyethylene (Fig. 6, entries 34, 36–40). As the Al/Zr molar ratio increased from 100 to 500, the catalytic activity rapidly increased from 2.8 × 10^5 to 11.0 ×10^5 g PE (mol of Zr)$^{-1}$ h^{-1}. Further increase of the Al/Zr molar ratio from 500 to 6000 resulted in a slightly increased catalytic activity. Meanwhile, the M_v value of

Table 3. Ethylene polymerization results catalyzed by zirconocenes **C5–C8**/MAO catalytic systems[a]

Entry	Catalyst	Al/Zr	Temp. (°C)	Time (min)	Pressure (MPa)	Yield (mg)	Activity[b]	M_V[c] (10^4 g mol^{-1})
23	Cp_2ZrCl_2	3000	80	30	0.6	815	16.3	12.7
24	Cp_2ZrCl_2	3000	80	60	0.6	831	8.3	12.5
25	Cp_2ZrCl_2	3000	110	30	0.6	1272	25.4	3.1
26	**C5**	3000	80	30	0.6	159	3.2	32.8
27	**C5**	3000	110	30	0.6	498	10.0	11.2
28	**C6**	3000	80	30	0.6	481	9.6	33.5
29	**C6**	3000	110	30	0.6	670	13.4	12.7
30	**C7**	3000	80	30	0.6	163	3.3	36.2
31	**C7**	3000	110	30	0.6	537	10.7	12.9
32	**C8**	3000	30	30	0.6	25	0.5	58.2
33	**C8**	3000	50	30	0.6	146	2.9	52.3
34	**C8**	3000	80	30	0.6	772	15.4	40.9[d]
35	**C8**	3000	110	30	0.6	1094	21.9	13.1[d]
36	**C8**	100	80	30	0.6	141	2.8	53.7
37	**C8**	300	80	30	0.6	358	7.2	51.0
38	**C8**	500	80	30	0.6	551	11.0	48.7
39	**C8**	1500	80	30	0.6	645	12.9	45.5
40	**C8**	6000	80	30	0.6	824	16.5	29.1
41	**C8**	3000	80	30	0.1	359	7.2	32.1
42	**C8**	3000	80	30	0.3	521	10.4	34.5
43	**C8**	3000	80	30	1.0	1378	27.6	42.0
44	**C8**	3000	80	5	0.6	125	15.0	23.2
45	**C8**	3000	80	10	0.6	267	16.0	27.6
46	**C8**	3000	80	15	0.6	409	16.4	32.5
47	**C8**	3000	80	45	0.6	1120	14.9	41.2
48	**C8**	3000	80	60	0.6	1380	13.8	43.7
49	**C8**	3000	80	90	0.6	1612	10.7	44.9
50	**C8**	3000	80	120	0.6	1771	8.9	47.1
51	**C8**	3000	80	180	0.6	1785	6.0	47.0

[a] Polymerization conditions: 1 μmol catalyst, solvent toluene (total volume 25 ml).

[b] Activity in 10^5 g PE (mol Zr)$^{-1}$ h^{-1}.

[c] Intrinsic viscosity was determined in decahydronaphthalene at 135 °C and molecular weight was calculated using the relation $[\eta] = 6.77 \times 10^{-4} M_v^{0.67}$.

[d] M_w and M_w/M_n were determined by GPC. For entry 34, $M_w = 45.7 \times 10^4$ g mol^{-1}, $M_w/M_n = 2.16$. For entry 35, $M_w = 11.5 \times 10^4$ g mol^{-1}, $M_w/M_n = 3.12$.

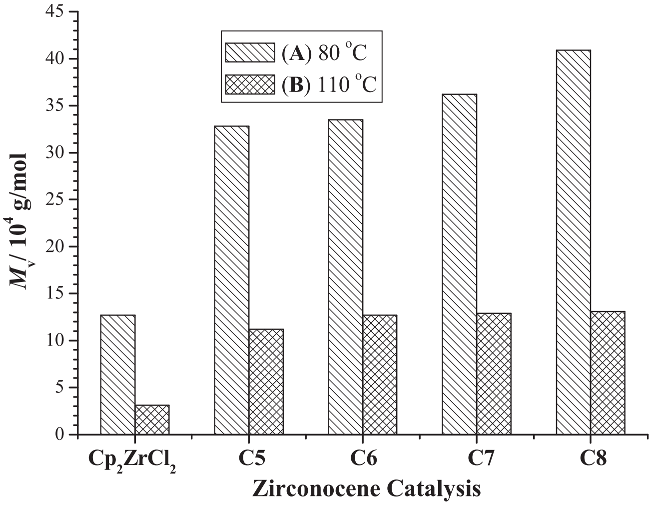


Figure 5. The viscosity average molecular weight (M_v) of polyethylene obtained by zirconocenes Cp_2ZrCl_2/MAO and **C5–C8**/MAO under different conditions. Polymerization conditions: (A) 80 °C (Table 3, entries 23, 26, 28, 30, 34); (B) 110 °C (Table 3, entries 25, 27, 29, 31, 35).

the resultant polyethylene decreased when the Al/Zr molar ratio increased due to the enhanced rate of chain transfer to aluminum for the termination. When the ethylene pressure was increased, both the catalytic activity and the molecular weight increased consistently (entries 34, 41—43).

The dependence of catalytic activities of **C8** on time is shown in Fig. 7 (entries 34, 44–51). At 80 °C, on prolonging the reaction time the catalytic activity increased in the early stage and then decreased slowly after 15 min. The highest activity of 16.4 × 10^5 g PE (mol Zr)$^{-1}$ h^{-1} was achieved in 15 min (entry 46). However, the polymer yield continuously increased from 409 to 1771 mg with polymerization time from 15 min to 2 h, while further enhancement of the polymerization time to 3 h resulted in a very slight increase of the polymers. This is presumably due to the limited ethylene uptake in the reaction mixture, because the polymerization mixture became more and more viscous after a long period of polymerization. These results indicate that the catalyst has a minimal lifetime of 2 h. In contrast, the typical Cp_2ZrCl_2 catalyst is short-lived. Under the same condition, no obvious increase in polyethylene yield was observed after 30 min.

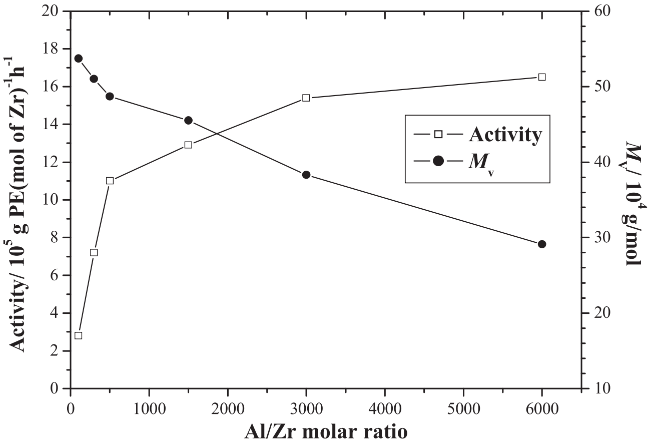


Figure 6. Plots of Al/Zr molar ratio versus catalytic activity (□) and viscosity average molecular weight (M_v) (●) of the polyethylene obtained by **C8**/MAO at 80 °C (Table 3, entries 34, 36–40).

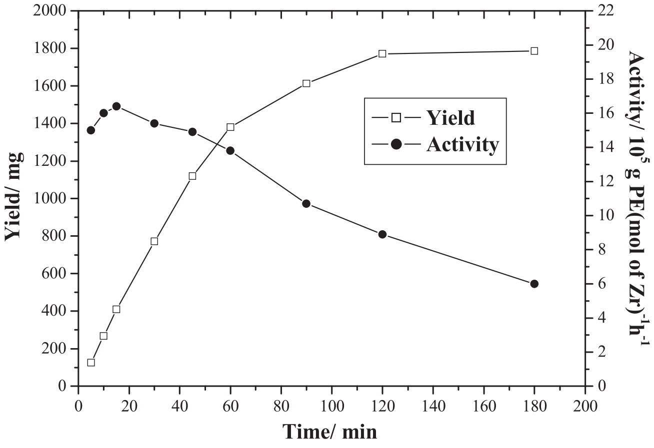


Figure 7. Plots of polymerization time versus catalytic activity (●) and polymer yield (□) of the resultant polyethylene obtained by zirconocene C8/MAO at 80°C (Table 3, entries 34, 44–51).

Polymer Analysis

^{13}C NMR analysis indicated that the resultant polyethylene is highly linear with no detectable branches (Fig. S1, supporting information). According to the results of differential scanning calorimetry (DSC), the obtained polyethylene showed high melting points (T_m) in the range of 133–145 °C, which also indicates that the polymer is a linear polyethylene.[25,28] In addition, the selected gel permeation chromatography (GPC) analysis of the resultant polyethylene revealed a narrow molecular weight distribution (M_w/M_n) (sample of entry 15, 2.32; sample of entry 17, 2.10; sample of entry 34, 2.16; sample of entry 35, 3.12), suggesting that the polyethylene is produced by a single active species (Figs S2–S5, supporting information).

Conclusions

In summary, we have developed a series of new titanocenes and zirconocenes (RCp)[Cp—(bridge)—(2-C_4H_3S)]MCl_2 bearing a pendant thiophene group on a Cp ring. Single-crystal X-ray diffraction analysis on titanocenes **C2** and **C4** revealed that both complexes exist in an expected coordination environment for a monomeric bent metallocene. In the presence of MAO, these monopendant thienyl-substituted titanocenes **C1–C4** and zirconocenes **C5–C8** showed a long catalytic lifetime and produced high- or ultra-high-molecular-weight polyethylene in comparison with Cp_2TiCl_2 and Cp_2ZrCl_2, respectively. This remarkable behavior may be attributed to the coordination of the thiophene group as a pendant donor which can stabilize the active catalytic species when these catalysts are activated by MAO. In addition, bulky substituents on the bridge unit of the thienyl-substituted Cp ring was beneficial to the catalytic activity of these titanocenes and zirconocenes.

Experimental

General Considerations

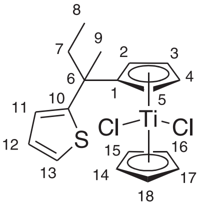
All manipulations of air- and/or moisture-sensitive compounds were performed under a dry argon atmosphere using standard Schlenk techniques unless otherwise noted. All solvents were refluxed over sodium/benzophenone ketyl or calcium hydride (CaH_2) and then freshly distilled under argon atmosphere before use. Methylaluminoxane (MAO) (1.5 M in toluene) was purchased from Sigma-Aldrich. Polymerization-grade ethylene was directly used without further purification. (MeCp)TiCl_3,[29] (^{n}BuCp)ZrCl_3·DME,[30] 2-thienyl lithium[14] and substituted fulvenes[31] were prepared by the literature procedures. All other chemicals were commercially available and used as received.

Measurements

NMR spectra of complexes were recorded on a Bruker Avance-400 spectrometer at ambient temperature, with $CDCl_3$ as the solvent (dried over CaH_2 for a minimum of 24 h and then distilled under argon atmosphere before use). Elemental analyses (C, H) were carried out on an EA-1106 type analyzer. IR spectra were recorded on a PerkinElmer System 2000 FT-IR spectrometer. ^{13}C NMR spectra of polyethylene were recorded on a Bruker Advance-500 spectrometer using 1,2-dichlorobenzene-d$_4$ as solvent at 100 °C. DSC trace and melting points of polyethylene were obtained from the second scanning run on a Universal V2.3C TA instrument at a heating rate of 10 °C min^{-1}. The intrinsic viscosities (η) of polyethylene were measured with an Ubbelohde viscometer in decahydronaphthalene at 135 °C and viscosity average molecular weight (M_v) was calculated as follows: $[\eta] = 6.77 \times 10^{-4}\ M_v^{0.67}$.[32] Molecular weights (M_n and M_w) and polydispersities (M_w/M_n) of polyethylene were determined by high-temperature GPC using a PL-GPC 220 instrument. The measurements were recorded at 150 °C using 1,2,4-trichlorobenzene as a solvent, at a flow rate of 1.0 ml min^{-1}. The calibration was made using polystyrene standard samples.

Synthesis of Group 4 Metallocenes (RCp)[Cp—(bridge)—(2-C_4H_3S)]MCl_2 (C1–C8)

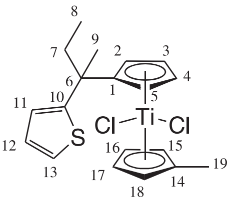
*Synthesis of Cp[Cp—C(MeEt) — (2-C_4H_3S)]TiCl_2 (**C1**)*



C1

To a solution of 2-thienyl lithium (1.621 g, 18.0 mmol) in diethyl ether (40 ml) was added dropwise a solution of 6-methyl-6-ethylfulvene (2.163 g, 18.0 mmol) in 10 ml diethyl ether at 0 °C, and the reaction mixture was warmed to ambient temperature and stirred overnight. The resulting precipitate was collected by filtration, washed with dried petroleum ether (20 ml) and dried under vacuum to afford lithium salt [Cp—C(MeEt)—(2-C_4H_3S)]Li (3.012 g, 14.3 mmol). The lithium salt (0.211 g, 1.0 mmol) was suspended in dried THF (20 ml) and added dropwise to a stirred solution of $CpTiCl_3$ (0.213 g, 1.0 mmol) in dried THF (20 ml) at −78 °C, and the reaction mixture was warmed to ambient temperature and stirred overnight. Then the solvent was removed under reduced pressure and the residue was washed with dried hexane (20 ml). The final product was crystallized from CH_2Cl_2/hexane by cooling at −30 °C. Titanocene **C1** was obtained as red crystals in 61.0% yield (0.236 g); m.p. 154−156 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, 1H, J = 5.1, 1.1 Hz, proton of C13), 7.02 (dd, 1H, J = 5.1, 3.6 Hz, proton of C12),6.92 (dd, 1H, J = 3.6, 1.1 Hz, proton of C11), 6.89 (m, 2H, protons of C3 and C4), 6.63 (m, 1H, proton of C2), 6.21 (s, 5H, protons of C14, C15, C16, C17 and C18), 6.08 (dd, 1H, J = 5.3, 2.9 Hz, proton of C5), 2.08 (m, 2H, protons of C7), 1.83 (s, 3H, protons of C9), 0.78 (t, 3H, J = 7.3 Hz, protons of C8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.55 (C10), 144.85 (C1), 127.41 (C12), 127.02 (C11), 125.31 (C13), 123.85 (C2), 122.37 (C5), 120.81 (C14, C15, C16, C17 and C18), 116.70 (C3), 113.69 (C4), 43.58 (C6), 38.37 (C7), 24.12 (C9), 9.14 (C8). IR (KBr, cm^{-1}): v = 3450 (w), 3089 (m), 2974 (m), 2920 (m), 2877 (w), 2858 (w), 1782 (w), 1469 (m), 1440 (m), 1378 (m), 1242 (w), 1049 (m), 1018 (m), 821 (vs), 705 (vs), 423 (m). Anal. Calcd for $C_{18}H_{20}Cl_2STi{\cdot}0.15CH_2Cl_2$: C, 54.51; H, 5.12. Found: C, 54.38; H, 5.17%. The final product contains about 0.15 equiv. of dichloromethane, as verified by NMR spectroscopy.

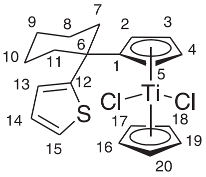
*Synthesis of (MeCp)[Cp—C(MeEt)—(2-C_4H_3S)]$TiCl_2$ (**C2**)*



C2

The procedure was similar to the synthesis of **C1**, using lithium salt [Cp—C(MeEt)—(2-C_4H_3S)]Li (0.586 g, 2.8 mmol) and (MeCp)$TiCl_3$ (0.652 g, 2.8 mmol). Titanocene **C2** was obtained as red crystals (suitable for X-ray diffraction) in 66.3% yield (0.745 g); m.p. 145–146 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, 1H, J = 5.1, 1.1 Hz, proton of C13), 7.00 (dd, 1H, J = 5.1, 3.6 Hz, proton of C12), 6.90 (dd, 1H, J = 3.6, 1.1 Hz, proton of C11), 6.84 (t, 2H, J = 2.4 Hz, protons of C3 and C4), 6.61 (dd, 1H, J = 5.1, 2.2 Hz, proton of C2), 6.07 (m, 2H, protons of C16 and C17), 5.94 (m, 2H, protons of C15 and C18), 5.76 (dd, 1H, J = 5.4, 2.9 Hz, proton of C5), 2.31 (s, 3H, protons of C19), 2.08 (m, 2H, protons of C7), 1.81 (s, 3H, protons of C9), 0.78 (t, 3H, J = 7.3 Hz, protons of C8). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.75 (C10), 144.22 (C1), 135.31 (C14), 126.96 (C12), 126.37 (C11), 125.19 (C13), 125.18 (C2), 124.60 (C5), 123.74 (C3), 121.49 (C4), 116.46 (C15), 116.06 (C18), 115.26 (C16), 113.19 (C17), 43.52 (C6), 38.33 (C7), 24.06 (C9), 16.47 (C19), 9.14 (C8). IR (KBr, cm^{-1}): v = 3450 (w), 3111 (m), 3093 (m), 2972 (s), 2919 (m), 2876 (w), 1495 (m), 1446 (m), 1371 (m), 1245 (w), 1224 (w), 1118 (m), 1048 (s), 828 (vs), 818 (vs), 717 (vs), 405 (m). Anal. Calcd for $C_{19}H_{22}Cl_2STi$: C, 56.88; H, 5.53. Found: C, 56.78; H, 5.64%.

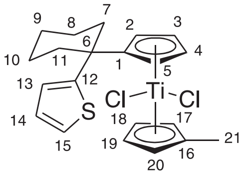
*Synthesis of Cp[Cp—C(cyclo-C_5H_{10})—(2-C_4H_3S)]$TiCl_2$ (**C3**)*



C3

The procedure was similar to the synthesis of **C1**, using lithium salt [Cp—C(*cyclo*-C_5H_{10})—(2-C_4H_3S)]Li (0.258 g, 1.1 mmol) and $CpTiCl_3$ (0.234 g, 1.1 mmol). Titanocene **C3** was obtained as red crystals in 70.6% yield (0.321 g); m.p. 152–154 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.28 (dd, 1H, J = 5.1, 1.1 Hz, proton of C15), 7.05 (dd, 1H, J = 5.1, 3.6 Hz, proton of C14), 6.94 (dd, 1H, J = 3.6, 1.1 Hz, proton of C13), 6.74 (t, 2H, J = 2.7 Hz, protons of C3 and C4), 6.46 (t, 2H, J = 2.7 Hz, protons of C2 and C5), 6.18 (s, 5H, protons of C16, C17, C18, C19 and C20), 2.55 (d, 2H, J = 13.3 Hz, protons of C7), 2.01 (m, 2H, protons of C11), 1.64 (m, 2H, protons of C8), 1.56 (m, 1H, proton of C10), 1.46 (m, 2H, protons of C9), 1.24 (m, 1H, proton of C10). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.18 (C12), 146.30 (C1), 127.34 (C14), 126.20 (C13), 124.27 (C15), 120.76 (C16, C17, C18, C19 and C20), 120.68 (C2 and C5), 118.98 (C3, C4), 44.28 (C6), 38.66 (C7 and C11), 25.54 (C9), 22.62 (C8 and C10). IR (KBr, cm^{-1}): v = 3425 (w), 3102 (m), 2933 (s), 2857 (m), 1654 (w), 1469 (m), 1444 (m), 1350 (w), 1262 (w), 1228 (w), 1073 (w), 1018 (m), 821 (vs), 711 (vs), 409 (m). Anal. Calcd for $C_{20}H_{22}Cl_2STi{\cdot}0.25CH_2Cl_2$: C, 55.98; H, 5.22. Found: C, 55.89; H, 5.45%. The final product contains about 0.25 equiv. of dichloromethane, as verified by NMR spectroscopy.

*Synthesis of (MeCp)[Cp—C(cyclo-C_5H_{10})—(2-C_4H_3S)]$TiCl_2$ (**C4**)*

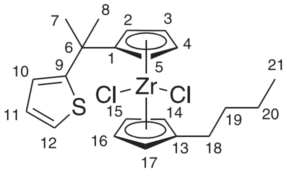


C4

The procedure was similar to the synthesis of **C1**, using lithium salt [Cp—C(*cyclo*-C_5H_{10})—(2-C_4H_3S)]Li (0.540 g, 2.3 mmol) and (MeCp)$TiCl_3$ (0.535 g, 2.3 mmol). Titanocene **C4** was obtained as red crystals (suitable for X-ray diffraction) in 58.6% yield (0.576 g); m.p. 186–187 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.27 (dd, 1H, J = 5.0, 1.0 Hz, proton of C15), 7.03 (dd, 1H, J = 5.0, 3.6 Hz, proton of C14), 6.92 (dd, 1H, J = 3.6, 1.0 Hz, proton of C13), 6.70 (t, 2H, J = 2.7 Hz, protons of C3 and C4), 6.42 (t, 2H, J = 2.7 Hz, protons of C2 and C5), 5.99 (t, 2H, J = 2.6 Hz, protons of C18 and C19), 5.80 (t, 2H, J = 2.6 Hz, protons of C17 and C20), 2.54 (d, 2H, J = 13.2 Hz, protons of C7), 2.31 (s, 3H, protons of C21), 2.01 (m, 2H, protons of C11), 1.64 (m, 2H, protons of C8), 1.56 (m, 1H, proton of C10), 1.46 (m, 2H, protons of C9), 1.23 (m, 1H, proton of C10). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.44 (C12), 145.68 (C1), 135.09 (C16), 127.33 (C14), 126.11 (C13), 125.02 (C2 and C5), 124.16 (C15), 119.87 (C3 and C4), 118.51

(C17 and C20), 115.55 (C18 and C19), 44.23 (C6), 38.62 (C7 and C11), 25.59 (C9), 22.66 (C8 and C10), 16.45 (C21). IR (KBr, cm^{-1}): *v* = 3448 (w), 3098 (m), 2927 (s), 2856 (m), 1497 (w), 1469 (w), 1440 (m), 1265 (w), 1240 (w), 1044 (m), 1018 (w), 846 (vs), 821 (vs), 708 (vs), 412 (w). Anal. Calcd for $C_{21}H_{24}Cl_2STi{\cdot}0.05CH_2Cl_2$: C, 58.59; H, 5.63. Found: C, 58.31; H, 5.58%. The final product contains about 0.04 equivalents of dichloromethane, as verified by NMR spectroscopy.

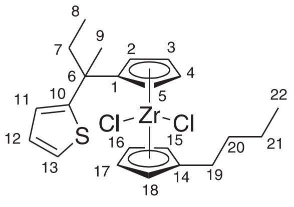
*Synthesis of (^{n}BuCp)[Cp—C(Me)$_2$—(2-C_4H_3S)]ZrCl$_2$ (**C5**)*



C5

The procedure was similar to the synthesis of titanocene **C1** (except that it was recrystallized from hexane), using lithium salt [Cp—C(Me)$_2$— (2-C_4H_3S)]Li (0.367 g, 1.90 mmol) and (^{n}BuCp) $ZrCl_3{\cdot}DME$ (0.785 g, 1.9 mmol). Zirconocene **C5** was obtained as a white solid in 40.3% yield (0.362 g); m.p. 117–118 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.16 (dd, 1H, *J* = 5.1 Hz, *J* = 1.0 Hz, proton of C12), 6.93 (dd, 1H, *J* = 5.1, 3.6 Hz, proton of C11), 6.81 (dd, 1H, *J* = 3.6, 1.0 Hz, proton of C10), 6.53 (t, 2H, *J* = 2.8 Hz, protons of C3 and C4), 6.32 (t, 2H, *J* = 2.8 Hz, protons of C2 and C5), 6.05 (t, 2H, *J* = 2.7 Hz, protons of C15 and C16), 5.99 (t, 2H, *J* = 2.7 Hz, protons of C14 and C17), 2.62 (t, 2H, *J* = 7.7 Hz, protons of C18), 1.83 (s, 6H, protons of C7 and C8), 1.51 (m, 2H, protons of C19), 1.32 (m, 2H, protons of C20), 0.90 (t, 3H, *J* = 7.3 Hz, protons of C21). ^{13}C NMR (100 MHz, CDCl$_3$) δ 155.51 (C9), 141.13 (C1), 135.79 (C13), 126.82 (C11), 123.54 (C10), 123.53 (C12), 117.79 (C2 and C5), 115.42 (C3 and C4), 113.89 (C14 and C17), 112.54 (C15 and C16), 39.36 (C6), 33.12 (C18), 31.17 (C19), 30.09 (C7 and C8), 22.59 (C20), 14.08 (C21). IR (KBr, cm^{-1}): *v* = 3449 (w), 3102 (w), 2963 (w), 2927 (w), 2856 (w), 1459 (w), 1381 (w), 1230 (w), 1040 (w), 847 (w), 820 (m), 707 (w). Anal. Calcd for $C_{21}H_{26}Cl_2SZr$: C, 53.37; H, 5.54. Found: C, 53.56; H, 5.50%.

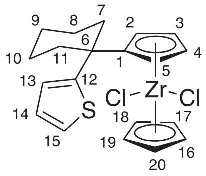
*Synthesis of (^{n}BuCp)[Cp—C(MeEt)—(2-C_4H_3S)]ZrCl$_2$ (**C6**)*



C6

The procedure was similar to the synthesis of titanocene **C1** (except that it was recrystallized from hexane), using lithium salt [Cp—C(MeEt)—(2-C_4H_3S)]Li (0.456 g, 2.2 mmol) and (^{n}BuCp) $ZrCl_3{\cdot}DME$ (0.897 g, 2.2 mmol). Zirconocene **C6** was obtained as a white solid in 44.5% yield (0.472 g); m.p. 94–95 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.23 (d, 1H, *J* = 5.0 Hz, proton of C13), 7.01 (t, 1H, *J* = 5.0 Hz, *J* = 4.8 Hz, proton of C12), 6.94 (d, 1H, *J* = 3.3 Hz, proton of C11), 6.60 (m, 2H, protons of C3 and C4), 6.49 (d, 1H, *J* = 2.5 Hz, proton of C2), 6.02 (m, 2H, protons of C16 and C17), 5.86 (m, 2H, protons of C15 and C18), 5.72 (dd, 1H, *J* = 5.3, 2.7 Hz, proton of C5), 2.59 (t, 2H, *J* = 7.7 Hz, protons of C19), 2.06 (m, 2H, protons of C7), 1.83 (s, 3H, protons of C9), 1.48 (m, 2H, protons of C20), 1.30 (m, 2H, protons of C21), 0.89 (t, 3H, *J* = 7.3 Hz, protons of C22), 0.77 (t, 3H, *J* = 7.3 Hz, protons of C8). ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.46 (C10), 141.02 (C1), 135.89 (C14), 126.99 (C12), 125.10 (C11), 123.73 (C13), 120.12 (C2), 118.42 (C5), 117.70 (C3), 116.18 (C4), 113.68 (C15), 112.94 (C18), 111.80 (C16), 109.56 (C17), 42.89 (C6), 38.65 (C7), 33.15 (C19), 30.04 (C20), 24.29 (C9), 22.58 (C21), 14.09 (C22), 9.25 (C8). IR (KBr, cm^{-1}): *v* = 3449 (w), 3105 (w), 2953 (w), 2924 (m), 2857 (w), 1491 (w), 1459 (w), 1412 (w), 1379 (w), 1241 (w), 1048 (m), 837 (m), 688 (m). Anal. Calcd for $C_{22}H_{28}Cl_2SZr$: C, 54.30; H, 5.80. Found: C, 54.21; H, 5.85%.

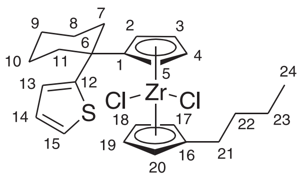
*Synthesis of Cp[Cp—C(cyclo-C_5H_{10})—(2-C_4H_3S)]ZrCl$_2$ (**C7**)*



C7

The procedure was similar to the synthesis of titanocene **C1** (except that it was recrystallized from toluene), using lithium salt [Cp—C(*cyclo*-C_5H_{10})—(2-C_4H_3S)]Li (0.728 g, 3.1 mmol) and $CpZrCl_3{\cdot}DME$ (1.090 g, 3.1 mmol). Zirconocene **C7** was obtained as a white solid in 35.1% yield (0.497 g); m.p. 216–217°. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.30 (dd, 1H, *J* = 5.1, 1.0 Hz, proton of C15), 7.07 (dd, 1H, *J* = 5.1, 3.6 Hz, proton of C14), 6.99 (dd, 1H, *J* = 3.6 Hz, *J* = 1.0 Hz, proton of C13), 6.53 (t, 2H, *J* = 2.8 Hz, protons of C3 and C4), 6.33 (t, 2H, *J* = 2.8 Hz, protons of C2 and C5), 6.10 (s, 5H, protons of C16, C17, C18, C19 and C20), 2.56 (d, 2H, *J* = 13.2 Hz, protons of C7), 1.98 (m, 2H, protons of C11), 1.64 (m, 2H, protons of C8), 1.57 (m, 1H, proton of C10), 1.47 (m, 2H, protons of C9), 1.24 (m, 1H, proton of C10). ^{13}C NMR (100 MHz, CDCl$_3$) δ 149.86 (C12), 143.03 (C1), 127.40 (C14), 126.13 (C13), 124.22 (C15), 116.38 (C16, C17, C18, C19 and C20), 115.50 (C2 and C5), 114.54 (C3 and C4), 43.48 (C6), 38.94 (C7 and C11), 25.63 (C9), 22.72 (C8 and C10). IR (KBr, cm^{-1}): *v* = 3425 (w), 3097 (w), 3065 (w), 2930 (m), 2857 (w), 1655 (w), 1443 (w), 1070 (w), 1018 (w), 838 (w), 816 (vs), 711 (s). Anal. Calcd for $C_{20}H_{22}Cl_2SZr$: C, 52.61; H, 4.86. Found: C, 52.58; H, 5.00%.

*Synthesis of (^{n}BuCp)[Cp—C(cyclo-C_5H_{10})—(2-C_4H_3S)]ZrCl$_2$ (**C8**)*



C8

The procedure was similar to the synthesis of titanocene **C1** (except that it was recrystallized from hexane), using lithium salt [Cp—C(*cyclo*-C_5H_{10})—(2-C_4H_3S)]Li (0.423 g, 1.8 mmol) and (^{n}BuCp)$ZrCl_3{\cdot}DME$ (0.740 g, 1.8 mmol). Zirconocene **C8** was obtained as a white solid in 39.1% yield (0.361 g); m.p. 116–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, 1H, J = 7.4 Hz, proton of C15), 7.05 (t, 1H, J = 4.8 Hz, proton of C14), 6.98 (d, 1H, J = 3.3 Hz, proton of C13), 6.50 (t, 2H, J = 2.6 Hz, protons of C3 and C4), 6.29 (t, 2H, J = 2.6 Hz, protons of C2 and C5), 5.93 (t, 2H, J = 2.5 Hz, protons of C18 and C19), 5.74 (t, 2H, J = 2.5 Hz, protons of C17 and C20), 2.59 (t, 2H, J = 7.7 Hz, protons of C21), 2.55 (d, 2H, J = 13.5 Hz, protons of C7), 1.99 (m, 2H, protons of C11), 1.64 (m, 2H, protons of C8), 1.56 (m, 1H, proton of C10), 1.48 (m, 4H, protons of C9 and C22), 1.30 (m, 2H, proton of C23), 1.23 (m, 1H, proton of C10), 0.89 (t, J = 7.4 Hz, 3H, proton of C24). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.09 (C12), 142.68 (C1), 135.67 (C16), 127.33 (C14), 125.97 (C13), 124.09 (C15), 118.15 (C2 and C5), 114.84 (C3 and C4), 114.25 (C17 and C20), 112.24 (C18 and C19), 43.44 (C6), 38.84 (C7 and C11), 33.14 (C21), 29.99 (C22), 25.65 (C9), 22.72 (C8 and C10), 22.57 (C23), 14.08 (C24). IR (KBr, cm^{-1}): v = 3448 (w), 3105 (w), 2927 (s), 2855 (m), 1492 (w), 1448 (w), 1413 (w), 1260 (w), 1044 (w), 935 (w), 840 (w), 812 (w), 688 (m). Anal. Calcd for $C_{24}H_{30}Cl_2SZr$: C, 56.22; H, 5.90. Found: C, 56.31; H, 5.99%.

X-Ray Crystallographic Studies

Single-crystal X-ray diffraction studies for titanocenes **C2** and **C4** were carried out on a Bruker AXSD8 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). All data were collected at 293 K using the ω-scan technique. Unit cell dimensions were obtained with least-squares refinements. Intensities were corrected for Lorentz and polarization effects and empirical absorption.[33] The structures were solved by direct methods[34] and refined by full-matrix least square on F^2.[34] All the calculations were carried out with the SHELXTL program. The thienyl residues in **C2** and **C4** were refined over two positions in a 0.60:0.40 ratio. Similarly, the terminal ethyl group in **C2** was refined over two positions (0.70:0.30). All non–hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized position.

General Procedure for Ethylene Polymerization

Ethylene polymerization was carried out in a 100 ml autoclave equipped with a magnetic stirrer. The autoclave was heated at 100 °C under vacuum for 30 min and then thermostated to the desired temperature and filled with ethylene. Appropriate amounts of MAO solution and toluene were added to the autoclave and was filled with ethylene for 15 min. After an appropriate amount of toluene solution of catalyst was injected to the reactor, ethylene at the desired pressure was introduced to start the polymerization. The reaction mixture was stirred vigorously for a designated time and the ethylene pressure in the autoclave was slowly vented. Then 10 ml ethanol was added to terminate the polymerization. The resulting mixture was poured into 3% HCl in ethanol (50 ml). The polymer was collected by filtration, washed with ethanol (30 ml × 2), and then dried for 16 h in a vacuum oven at 60 °C to constant weight.

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