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Self-immobilized metallocene catalysts bearing an allyl group for ethylene polymerization, X-ray crystal structure of $[(CH_2{=}CHCH_2)CH_3Si(C_{13}H_8)_2]ZrCl_2$

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Abstract

A series of *ansa*-metallocene complexes with an allyl substituted silane bridge $[(CH_2{=}CHCH_2)CH_3Si(C_5H_4)_2]TiCl_2$ (**1**), $[(CH_2{=}CHCH_2)CH_3Si(C_9H_6)_2]MCl_2$ [M = Ti (**2**), Zr (**3**), Hf (**4**)] and $[(CH_2{=}CHCH_2)CH_3Si(C_{13}H_8)_2]ZrCl_2$ (**6**) have been synthesized and characterized. The molecular structure of **6** has been determined by X-ray crystallographic analysis. Complexes **1**–**4**, **6** bearing allyl groups have been investigated as self-immobilized catalysts for ethylene polymerization in the presence of MMAO. The results showed that the self-immobilized catalysts **1**–**4**, **6** kept high ethylene polymerization activities of ca. 10^6 g PE mol^{-1} M h^{-1} and high molecular weight ($M_w \approx 10^5$) of polyethylene.

Keywords: Allyl group; *ansa*-Metallocene catalysts; Self-immobilization; Ethylene polymerization; X-ray structure analysis

1. Introduction

Metallocene catalysts gained widespread importance for polymerization of olefins on account of their high activity and versatility [1–3]. Metallocene catalysts show a single site active centre in homogeneous phase and make it possible to tailor the structure of polymers in a precise way. Great industrial interest has arisen in employing them in existing technical process (drop-in technology) to replace the conventional heterogeneous catalysts.

In order to be applied in the conventional gas phase or slurry reactors, homogeneous catalysts have to be heterogenized because soluble catalysts would cause "fouling" which means the formed polyolefin is deposited at the reactor walls and caused "boiler scale effect". The inorganic supports such as silica or alumina [4] and also organic supports such as polystyrene and starch [5], have been used to heterogenize soluble polymerization catalysts. Many research groups reported the heterogenization of metallocene catalysts [6]. As a different heterogenization strategy, Alt. et al. developed the self-immobilization of metallocene catalysts, which means to synthesize metallocene catalysts with an olefin or alkyne function that can be used as a comonomer in the polymerization process [7]. Recently our group [8] and Herrmann et al. [9] reported, respectively, on the self-immobilization of Ti, Ni and Fe catalysts for olefin polymerization. The homogenous self-immobilized catalyst could be transferred to a heterogeneous catalyst by itself during the ethylene polymerization. Herein, we report a series of metallocene complexes with an allyl substituted silane bridge as self-immobilized catalysts as well as their catalytic performance for ethylene polymerization. In addition, a molecular structure of complex **6** has been characterized by X-ray crystallographic analysis.

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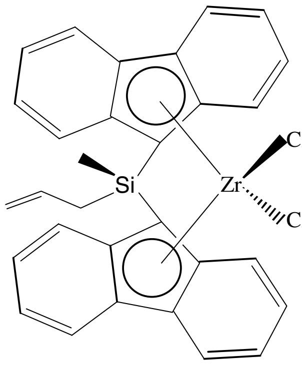

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2. Results and discussion

2.1. Synthesis of the ansa-metallocene complex *1*

The *ansa*-metallocene complex **1** was synthesized via a modified literature procedure [10,11]. The silylene-bridged ligand precursor was easily obtained from the allyldichloromethylsilane and cyclopentadienyl sodium, and used without further purification. Treatment of a solution of ^{n}BuLi with the bridged ligand produced the dilithium salt. The titanium complex resulted from the reaction of $TiCl_4$ with the resulting dilithium salt (Scheme 1).

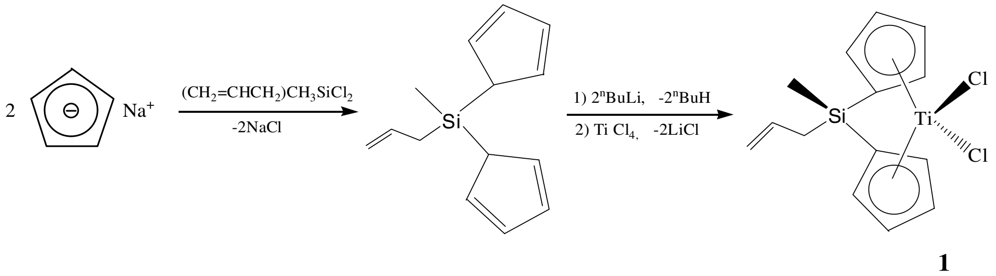
The ^{1}H NMR spectra measured for complex **1** exhibited the characteristic AA′BB′ pattern expected for the cyclopentadienyl ring protons. The chemical shift patterns with two resonances at 6.00–6.06 ppm and two resonances at 7.18–7.25 ppm, observed for the cyclopentadienyl protons of complex **1**. Compared with its analogous zirconium complex [11], all chemical shifts of complex **1** shift to the low field.

2.2. Synthesis of the ansa-metallocene complexes *2–4*

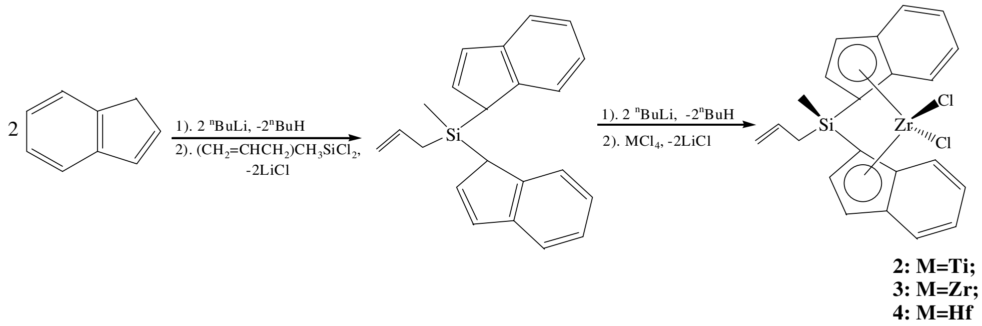
The bridged indenyl metalllocene complexes were synthesized according to well known procedures [12–14].The indenyllithium salt was reacted with the corresponding silane in diethyl ether to form the ligand precursor. In a second step, the ligand precursor at low temperature was reacted with two equivalents ^{n}BuLi to produce the dilithium salt. Finally, the dithium salt was reacted with MCl_4 (M = Ti, Zr, Hf) to give the corresponding *ansa*-metallocene complexes (Scheme 2).

2.3. Synthesis of the ligand (*5*) and the ansa-metallocene catalyst (*6*)

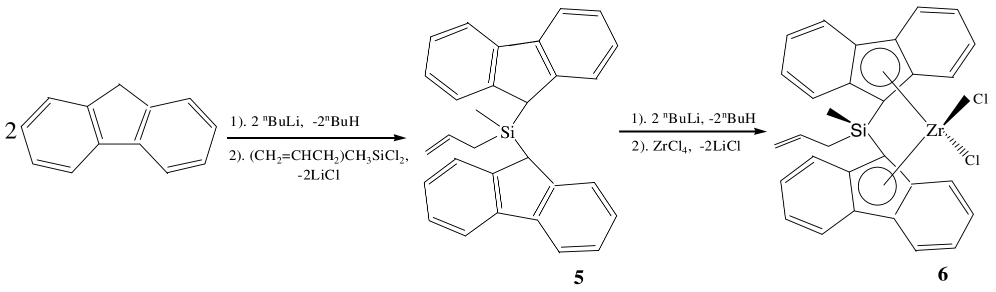
The procedures employed to synthesize **5** and **6** were modified from that described in the literature [15,16]. The ligand precursor **5** was prepared by reacting 2 equiv. fluorenyllithium salt with alllyldichloromethylsilane. The bridged ligand was then converted to its



Scheme 1. Synthesis of metallocene catalyst **1**.



Scheme 2. Synthesis of metallocene catalysts **2**–**4**.



Scheme 3. Synthesis of metallocene catalyst **6**.

corresponding zirconocene according to Scheme 3. In fact, complex **6** can be obtained directly from precursor **5** reacting *n*-butyl lithium and then with $ZrCl_4$ without further purification. Complex **6** in both solution and solid is unstable at temperature over 60 °C even under argon atmosphere, its solid gradually transform from red color into the orange color.

3. Molecular structure of 6

The molecular structure of allylmethylsilylene-bis(9-fluorenyl)zirconium dichloride(**6**) was determined by single crystal X-ray diffraction. Suitable crystal was obtained by slow diffusion hexane into a toluene solution at low temperature. As depicted in Fig. 1, the geometry around the Zr atom is distorted tetrahedron formed by two fluorenyl rings and two Cl atoms. The Zr atom, Si atom and two bridge-head carbon atoms are in the same plane. The Zr–Cl bond lengths amount to 2.3912(11) (Zr–Cl(1)) and 2.4075(11) Å (Zr–Cl(2)). The Cl(1)–Zr–Cl(2) angle is 95.39(5)°, and the Cp(1)–Zr–Cp(2) angle is 65.76°. The bond lengths between zirconium and the carbon atoms of the fluorenyl rings are in a range between 2.434(3) and 2.685(3) Å (C(1)–C(5)) and 2.415(3) and 2.734(4) Å (C(14)–C(18)), respectively.

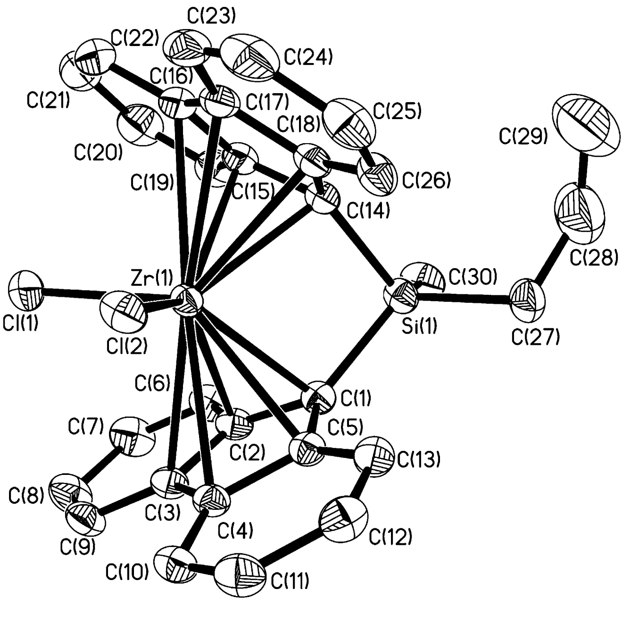


Fig. 1. Molecular structure of **6**. Cp(1) and Cp(2) define the centroids of the fluorenyl ring atoms C(1)–C(5) and C(14)–C(18), respectively. Selected bond lengths (Å) and angles (°): Zr–Cl(1) 2.3912(11), Zr–Cl(2) 2.4075(11), Zr–Cp(1) 2.271, Zr–Cp(2) 2.294, Si–C(1) 1.872(3), Si–C(14) 1.869(4), Si–C(27) 1.870(4), Si–C(30) 1.867(4), C(28)–C(29) 1.326(11), Cl(1)–Zr–Cl(2) 95.39(5), Cp(1)–Zr–Cp(2) 65.76°, C(1)–Si–C(14) 95.52(15), C(27)–Si–C(30) 104.6(2), Si–C(27)–C(28) 109.0(4), C(27)–C(28)–C(29) 127.2(8).

4. Catalytic activity

In the presence of a cocatalyst (MMAO), all synthesized *ansa*-metallocene catalysts have been tested by ethylene polymerization. In Table 1, the detailed data of ethylene polymerization are listed. For catalyst **3**, the data show that the increment of $n(\mathrm{Al})/n(\mathrm{Zr})$ leads to increase in activity, but excess MMAO may deactivate the active center, and thus the activity decrease. The effect of temperature on the activity is similar with that of $n(\mathrm{Al})/n(\mathrm{Zr})$. Too high temperature can deactivate the active centers and decrease the solubility of ethylene in toluene.

Table 1
Ethylene polymerization results of self-immobilized catalysts

Run	Catalyst (μmol)	*T* (°C)	$n(\mathrm{Al})/n(\mathrm{M})$	Pressure (atm)	Activity[a]
1	**3**(1.0)	10	1500	1.0	1.09
2	**3**(1.0)	10	2000	1.0	1.99
3	**3**(1.0)	10	2500	1.0	2.38
4	**3**(1.0)	10	3000	1.0	1.83
5	**3**(1.0)	10	3500	1.0	1.20
6	**3**(1.0)	0	2500	1.0	0.98
7	**3**(1.0)	25	2500	1.0	3.24
8	**3**(1.0)	40	2500	1.0	4.51
9	**3**(1.0)	55	2500	1.0	3.02
10[b]	**3**(10)	40	2500	4.0	10.51
11	**1**(2.0)	26	2200	1.0	0.31
12	**2**(2.0)	26	2200	1.0	2.12
13	**4**(2.0)	26	2200	1.0	1.98
14	**6**(2.0)	26	2200	1.0	3.56

[a] 10^6g PE mol^{-1}M h^{-1} (M = Ti, Zr, Hf).
[b] Toluene 150 ml.

Compared run 8 with run 10, we find that the high ethylene pressure can intensely enhance the activity.

The complexes **2**–**4** and **6** have higher polymerization activities than the complex **1**. The results can be related with the ability of the catalyst to copolymerize. In fact, we found that the ability of the complex **1** to copolymerize with ethylene was poor than other complexes. In addition to, because of self-immobilization, these synthesized *ansa*-metallocene catalysts can keep high activity for ethylene polymerization when MMAO was used in the course of polymerization.

A part of polymers were characterized by DSC and GPC (Table 2). The melting points of polyethylenes are in the range of 131.5–136.4 °C. Most of these polyethylenes have melting points around 135 ± 1 °C. The corresponding fusion enthalpy values of 152–178 J g^{-1} indicate crystallinity degrees of 53–61%. The polymer obtained from complex **6** has the highest melting point and the highest crystallinity degrees. The narrow polydispersity of polymers indicates the single active center during the course of ethylene polymerization. The bulk density of PE produced by these catalysts are in the range of 0.113–0.242 g/cm^{-1}. In order to improve the morphology of polymer products, catalysts **1**–**4**, **6** were co-polymerized with styrene to generate polymerized metallocene catalysts and corresponding SiO_2-supported core-shell catalysts. Further investigation of these aspects are in progress [8c,11].

Table 2
The results of DSC and GPC

Run	T_m[a] (°C)	ΔH_m[b] (J/g)	χ_c[c] (%)	M_η (g/mol)	M_w (g/mol)	M_w/M_n
3	135.89	157.47	54		313,000	2.42
8	135.39	159.62	55	n.d.[d]	n.d.	
10	134.45	153.76	53		501,000	2.52
11	135.66	152.78	53	n.d.	n.d.	
12	133.07	156.66	54	500,000		
13	131.53	173.16	60	132,000		
14	136.43	178.19	61	320,000		

[a] The values of the melting peak of the second heating course of the DSC were selected as melting point.

[b] The values of the second heating course of the DSC were indicated as fusion enthalpies ΔH_m.

[c] The crystallinity degree, $\chi_c = \Delta H_m/\Delta H_m^0$.

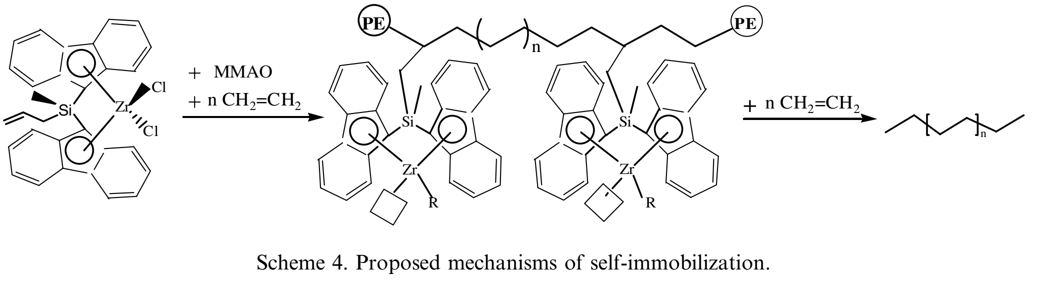
[d] Not determined.

As expected the phenomena of self-immobile effect similar to the neutral, single-component nickel catalysts [8] could be observed during the polymerization processes using catalysts **1**–**4**, **6**. The proposed mechanism of the self-immobilization was that as soon as ethylene is applied to the solution of the self-immobilized metallocene catalyst in the presence of co-catalyst (MMAO), ethylene is polymerized and catalyst molecules were simultaneously incorporated into the growing polymer due to their allyl function (Scheme 4). To further study the self-immobilization, the red insoluble particles from self-immobilized metalocene catalysts, obtained during the initial stage of polymerization, were separated to be used as heterogeneous catalysts for ethylene polymerization and they still displayed high activities [17]. That is to say, after self-immobilized catalyst molecules were incorporated into the growing polymer the centers of the catalyst were still active. Thus the homogeneous catalysts had been transferred to a heterogeneous system by itself without any supports. And active centers distributed on the polymer chain could prevent catalysts losing effectiveness and benefit to make efficient use of their catalytic activities.

5. Experimental

5.1. General procedures

All operations were carried out under purified argon atmosphere using Schlenk techniques. Solvents were dried over Na/benzophenone and distilled prior to use. Indene (Ind, Aldrich) was distilled from CaH_2. Fluorene (Flu, Fluka), $(CH_2{=}CHCH_2)CH_3SiCl_2$ (Aldrich), ^nBuLi (1.6 M in hexane, Aldrich), $TiCl_4$ (Beijing, China), $ZrCl_4$ (Aldrich), $HfCl_4$ (ACROS) were purchased from Aldrich and used without further purification. Modified methylaluminoxane (MMAO) was purchased from Acros Organics as 10% weight of a toluene solution and used without further purification. The cyclopentadienyl sodium (CpNa) was prepared according to literature procedure [18]. IR spectra were recorded on Bio-Rad FT-135 spectrometer. The ^1H NMR spectra were recorded on a Bruker 300 spectrometer. Elemental



Scheme 4. Proposed mechanisms of self-immobilization.

analyses were recorded on an elemental Vario EL spectrometer.

5.2. *Allylmethylsilylene-bis(1-cyclopentadienyl)titanium dichloride (**1**)*

To a solution of CpNa/THF (1.6 ml, 4.0 mmol) in 30 ml dimethoxyethane (DME) at −78 °C was added slowly allyldichloromethylsilane (0.29 ml, 2.0 mmol). The suspension was stirred overnight at room temperature. The mixture was cooled to −78 °C, and to this was added dropwise a solution of ^{n}BuLi in hexane (2.5 ml, 4.0 mmol). The resulting suspension was warmed to room temperature and kept to stir overnight. The mixture was transferred to a DME solution of $TiCl_4$ (0.22 ml, 2.0 mmol) at −78 °C. The suspension was allowed to stir for 48 h, and the solvent was removed under vacuum. The residue was extracted in toluene and cooling the filtrate at −25 °C gave complex **1** (0.20 g, 31%) as a brown crystals. IR (KBr, cm^{-1}) ν: 3100, 3078, 2956, 2924, 2880, 1629, 1450, 1415, 1374, 1316, 1254, 1176, 1128, 1044, 899, 816, 784. ^1H NMR ($CDCl_3$, ppm): δ 7.25 (t, 2H, C_5H_4–βH), 7.18 (t, 2H, C_5H_4–βH), 6.06 (t, 2H, C_5H_4–αH), 6.00 (t, 2H, C_5H_4–αH), 5.95 (m, 1H, –CH=), 5.23 (m, 1H, CH_2=), 5.14 (m, 1H, CH_2=), 2.35 (d, 1H, –CH_2–), 2.25 (d, 1H, –CH_2–), 0.71 (s, 3H, $SiCH_3$). ^{13}H NMR ($CDCl_3$, ppm): δ 0.90(CH3), 22.4(CH2), 110.4 (=CH2), 134 (=CH), 132.0, 122.1, 18.0. Anal. Calc. for $C_{14}H_{16}Cl_2SiTi$: C, 50.79; H, 4.84. Found: C, 50.55; H, 4.70%.

5.3. *Allylmethylsilylene-bis(1-indenyl)titanium dichloride (**2**)*

To a solution of indene (0.47 ml, 4.0 mmol) in 30 ml hexane at 0 °C was slowly added a solution of ^{n}BuLi in hexane (2.5 ml, 4.0 mmol). The suspension was stirred overnight at room temperature. The mixture was separated by centrifugation and the solid was washed with hexane. The white solid was dried in vacuo for 6 h. The solid was dissolved in diethyl ether (Et_2O) and to this was added slowly allyldichloromethylsilane (0.29 ml, 2.0 mmol) at −78 °C. The mixture was then stirred for 12 h at room temperature. The Li salts were removed by centrifugation and to the upper clear solution was added dropwise at −78 °C to a solution of ^{n}BuLi in hexane (2.5 ml, 4.0 mmol). After 12 h stirring, the solvent was removed, and the solid was washed with hexane and dried in vacuo for 5 h. The dilithium salt was dissolved in Et_2O and a solution of $TiCl_4$ (0.22 ml, 2.0 mmol) in Et_2O was added at −78 °C. The suspension was stirred for 48 h. The solvent was removed under vacuum and the residue was extracted in toluene. The solid residue was washed twice with hexane (30 ml) and dried in vacuo to yield **2** as a red solid (0.34 g, 40%). IR (KBr, cm^{-1}) ν: 3360, 3059, 3011, 2947, 1793, 1623, 1592, 1529,1452, 1403, 1384, 1335, 1252, 1210, 1187, 1155, 1096, 1027, 1006, 956, 918, 872, 778, 763, 529, 464. ^1H NMR ($CDCl_3$, ppm): δ 7.86–7.24 (m, 8H, aromH), 7.17(d, 2H, β-IndH), 6.90 (d, 2H, α-IndH), 6.36 (m, 1H, CH=), 5.90 (m, 2H, CH_2=), 2.90 (m, 2H, –CH_2–), 1.27 (s, 3H, $SiCH_3$). Anal. Calc. for $C_{22}H_{20}Cl_2SiTi$: C, 61.28; H, 4.64. Found: C, 61.59; H, 4.82%.

5.4. *Allylmethylsilylene-bis(1-indenyl)zirconium dichloride (**3**)*

Following the procedure described for **2**, indene (0.47 ml, 4.0 mmol), 1.6M ^{n}BuLi (2.5 ml), allyldichloromethylsilane (0.29 ml, 2.0 mmol), ^{n}BuLi (2.5 ml, 4.0 mmol) and $ZrCl_4$ (0.466 g, 2.0 mmol) gave **3** (0.43 g, 46%) as a red/orange solid. IR (KBr, cm^{-1}): 3366, 3072, 2956, 1794, 1629, 1602, 1528, 1448, 1417, 1386, 1341, 1295, 1253, 1212, 1192, 1162, 1149, 1080, 1025, 993, 964, 932, 811, 772, 751, 717, 578, 453. ^1H NMR ($CDCl_3$, ppm): δ 7.53–7.15 (m, 8H, aromH), 6.98(d, 2H, β-IndH), 6.75 (d, 2H, α-IndH), 5.76 (m, 1H, CH=), 4.91(m, 2H, CH_2=), 1.82 (m, 2H, –CH_2–), 0.93 (s, 3H, $SiCH_3$). Anal. Calc. for $C_{22}H_{20}Cl_2SiZr$: C, 55.68; H, 4.22. Found: C, 55.35; H, 4.06%.

5.5. *Allylmethylsilylene-bis(1-indenyl)hafnium dichloride (**4**)*

Analogous to the synthesis of **2** but using indene (0.47 ml, 4.0 mmol), 1.6M ^{n}BuLi (2.5 ml), allyldichloromethylsilane (0.29 ml, 2.0 mmol), ^{n}BuLi (2.5 ml, 4.0 mmol) and $HfCl_4$ (0.641 g, 2.0 mmol) gave **4** (0.42 g, 37%) as orange crystals. IR (KBr, cm^{-1}) ν: 3361, 3075, 2960, 1796, 1630, 1601, 1532, 1453, 1416, 1385, 1339, 1301, 1255, 1217, 1199, 1163, 1100, 1029, 1005, 970, 945, 823, 775, 764, 580, 478. ^1H NMR ($CDCl_3$, ppm): δ 7.50–6.93 (m, 8H, aromH), 6.57 (d, 2H, β-IndH), 6.32 (d, 2H, α-IndH), 5.31 (m, 1H, CH=), 4.75 (m, 2H, CH_2=), 1.34 (m, 2H, –CH_2–), 0.85 (s, 3H, $SiCH_3$). Anal. Calc. for $C_{22}H_{20}Cl_2SiHf$: C, 47.03; H, 3.56. Found: C, 47.35; H, 3.67%.

5.6. *Bis(9-fluorenyl)allylmethylsilane (**5**)*

To a solution of fluorene (0.665 g, 4.0 mmol) in 30 ml Et_2O at 0 °C was added dropwise a solution of ^{n}BuLi in hexane (2.5 ml, 4.0 mmol). The solution was stirred overnight at room temperature. Allyldichloromethylsilane (0.29 ml, 2.0 mmol) was slowly added at −78 °C. The mixture was stirred for 14 h at room temperature and hydrolyzed with aqueous NH_4Cl. The ether phase was separated and the aqueous layer was extracted with Et_2O. The combined ether phases were dried over $MgSO_4$. The solvent was removed under reduced pressure. The solid was washed with hexane and recrystallized from 1:1 toluene/hexane to give **5** (0.66 g, 80%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$, ppm): δ 7.86–7.22 (m, 16H, aromH), 4.95 (m, 1H, CH=), 4.51 (m, 2H, CH_2=), 4.05 (s, 2H, CH_{Flu}), 1.35 (m, 2H, –CH_2–), −0.28 (s, 3H, $SiCH_3$). Anal. Calc. for $C_{30}H_{26}Si$: C, 87.38; H, 5.83; Found: C, 87.25; H, 5.77%.

5.7. Allylmethylsilylene-bis(9-fluorenyl)zirconium dichloride (**6**)

To a solution of **5** (0.83 g, 2.0 mmol) in 30 ml DME at −78 °C was added dropwise two equivalents of a solution of ^{n}BuLi in hexane (2.5 ml, 4.0 mmol). The solution was stirred overnight at room temperature. A solution of $ZrCl_4$ (0.466 g, 2.0 mmol) in DME was added at −78 °C. The resulting suspension was stirred for 40 h and the solvent was removed under vacuum. The residue was extracted in toluene to remove LiCl salt. Evaporation in vacuo gave red solid and washed with hexane several times. Recrystallization from Toluene/hexane afforded red crystals of **6** (0.32 g, 28%). IR (KBr, cm^{-1}) ν: 3392, 3059, 2926, 1630, 1473, 1445, 1384, 1324, 1252, 1192, 1155, 1080, 1029, 894, 812, 782, 738, 695, 612, 496, 456. ^{1}H NMR ($CDCl_3$, ppm): δ 7.87–7.22 (m, 16H, aromH), 4.99 (m, 1H, CH=), 4.59 (m, 2H, CH_2=), 1.35 (m, 2H, –CH_2–), −0.44 (s, 3H, $SiCH_3$). Anal. Calc. for $C_{30}H_{24}Cl_2SiZr$: C, 62.70; H, 4.18. Found: C, 62.61; H, 4.13%.

5.8. X-ray crystal structure analysis for **6**

Single crystals were sealed in thin-walled glass capillaries under argon atmosphere. The intensity data of the single crystal was collected on the CCD-Bruker Smart APEX system. The determinations of unit cell and intensity data were performed with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All the data were collected at room temperature using the ω scan technique. Herein we provide information on the data collection and refinement parameters for complex **6**. Selected bond lengths and angles are given in Fig. 1 and Section 6.

Complex **6**$\cdot C_7H_8$: $C_{33.5}H_{28}Cl_2SiZr$, $M_r = 620.77$. Crystal system: triclinic, space group: $P\bar{1}$. Unit cell dimension: $a = 9.768(4)$ Å, $b = 11.282(5)$ Å, $c = 13.814(6)$ Å, $\alpha = 99.040(5)°$, $\beta = 108.509(5)°$, $\gamma = 97.588(5)°$; unit cell volume $V = 1398.6(10)$ Å^3 and $Z = 2$. Crystal size: $0.30 \times 0.20 \times 0.15$ mm, $D_c = 1.474$ g cm^{-1}. 2θ range: $3.18° \leqslant 2\theta \leqslant 50.02°$. Reflections collected: 5829, reflections unique: 4822, data/restraints/parameter: 4822/6/353. Goodness-of-fit: 1.108. R_1 observed/all data: 0.0403/0.0481, wR_2 observed/all data: 0.1092/0.1167.

5.9. Polymerization of ethylene

A 200 ml Schlenk-type glass reactor containing 50 ml toluene was equilibrated with the ethylene monomer. MMAO were added as a solution in toluene. After stirred for 5 min, the appropriate catalyst solution in toluene was added. After reaction for 1 h, the polymerization was terminated with an ethanol solution containing 1% HCl. The mixture was filtered, washed and dried in a vacuum at 40 °C for 24 h.

5.10. Polymer analysis

Melting points were determined by DSC with a Perkin–Elmer 7 series Thermal Analysis System. About 5 mg of each of the polymers were fused into standard aluminum pans and measured using the following temperature program: first heating phase (10 K/min) from 50 to 150 °C, cooling phase (10 K/min) to 50 °C, second heating phase (10 K/min) from 50 to 150 °C. Molecular weights of parts of polymers were determined by Gel Permeation Chromatograph using PL-GPC 220 of Changchun Institute of Applied Chemistry (solution in 1,2,4-trichlorobenzene at 150 °C). Others were determined using an Ubbelohde precision capillary viscometer in *cis*/*trans* decalin at 135 °C.

6. Supplementary material

Crystallographic data of the structural analysis for **6** have been deposited with the Cambridge Crystallographic Data Center, CCDC no 221577. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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