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Silylene-bridged fluorenyl-containing ligands and zirconium complexes with C_1 and C_s symmetry: general synthesis and olefin polymerization catalysis ☆

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Abstract

A variety of new silylene-bridged fluorenyl-containing ligands has been synthesized with good yields via a convenient synthetic route. Two dimethylsilylene-bridged (η^5-indenyl)(η^5-fluorenyl) (1) and (η^5-cyclopentadienyl)(η^5-fluorenyl) (2) zirconocene dichlorides with C_1 and C_s molecular symmetry have also been prepared. Upon activation with methyl aluminoxane, the former produced a polypropylene of high molecular weight, but with low activity and isotacticity. The latter catalyzed non-stereospecific propylene polymerization without any syndiotactic tendency, but with 40 and 20 times greater ethylene and propylene activity respectively than the former catalytic system.

Keywords: Zirconium; Olefin; Polymerization catalysis; Fluorenyl ligands

1. Introduction

There is intense current research interest in Group 4 metallocene complexes because they are catalyst precursors for aspecific [1], isospecfic [2] and syndiospecific [3] olefin polymerizations. Perfectly atactic polypropylene (*a*-PP) was obtained by ethylene-bis(fluorenyl)zirconium dichloride with a high activity *A* of polymerization and low rate of β-hydride chain transfer [1d]. With replacement of $-C_2H_4-$ by $Me_2Si<$, the dimethylsilylene-bridged derivative [1c] produces *a*-PP with even higher molecular weight (MW). *rac*-Ethylene-bis(indenyl)zirconium dichloride produces isotactic polypropylene (*i*-PP) with respect to methyl aluminoxane (MAO)-activated [2] or $Ph_3CB(C_6F_5)_4$-activated [4] systems. The silylene bridged analog again exhibited increased isotacticity and MW of *i*-PP [4b,5] relative to the ethylene bridged precursor.

Isopropylidene-(η^5-cyclopentadienyl)(η^5-fluorenyl)zirconium dichloride with C_s symmetry was discovered by Ewen et al. [3a] to catalyze the syndiospecific polymerization of propylene at an elevated temperature T_p of polymerization with *A* suitable for the manufacture of syndiotactic polypropylene (*s*-PP). Replacement of the two methyl groups on the carbon bridge with either two phenyl groups [3b] or ^{t}Bu and H [3c] groups improved the stereoregularity and MW of *s*-PP. It is note worthy that, although the latter precursor does not have C_s symmetry, the chiral neopentylidene derivative was found to have virtually the same polymerization behaviors [3c] as the other two. This observation thus demonstrates that it is the local molecular symmetry rather than the global symmetry that controls the stereochemistry of propagation.

Current synthetic methods toward the synthesis of either C_1 or C_s symmetric Group 4 metallocenes are based on the reaction of fluorenyllithium and 6,6-dialkyl fulvenes [3], which is restricted to variation in substituents on the bridge carbon atom. One objective of our current research is to design a general synthetic route toward the synthesis of silylene-bridged fluorenyl-containing ligands and subsequently the corresponding silylene bridged zirconium complexes. A C_1-symmetric dimethylsilylene-(η^5-indenyl)(η^5-fluorenyl)zirconium dichloride (1) and a C_s-symmetric

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☆ Dedicated to Professor H.-H. Brintzinger on the occasion of his 60th birthday.

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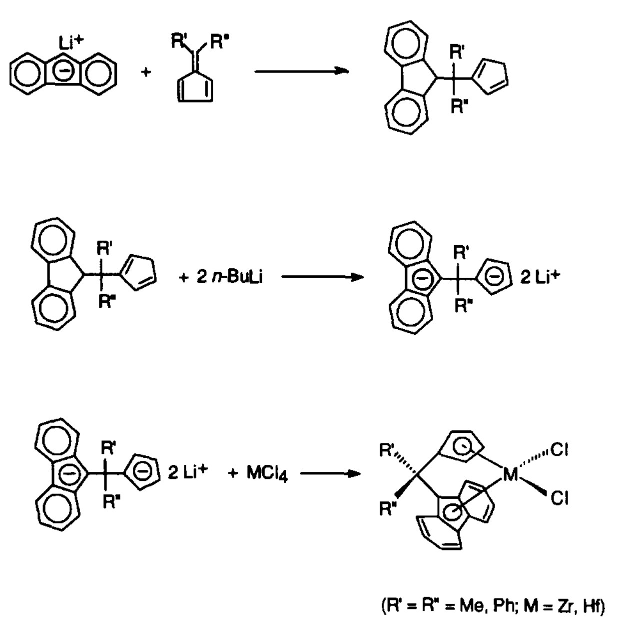
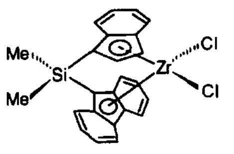


(R' = R" = Me, Ph; M = Zr, Hf)

Scheme 1.

dimethylsilylene-(η^5-cyclopentadienyl)(η^5-fluorenyl) zirconium dichloride (**2**) have thus been synthesized, and their Ziegler–Natta polymerization behaviors have been investigated.



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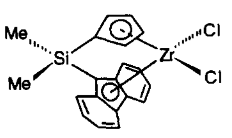


2

2. Results and discussion

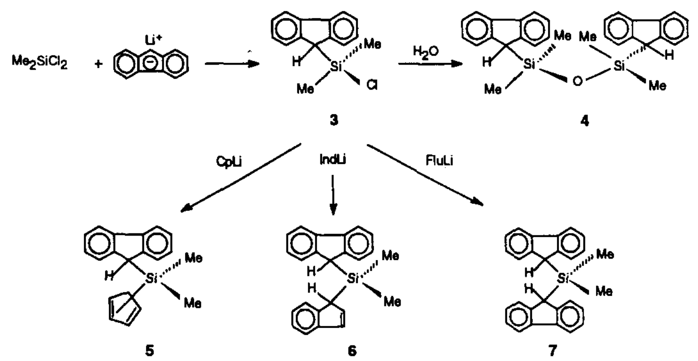
The traditional synthetic route leading to C_s-symmetric *ansa*-metallocenes is depicted in Scheme 1. The same approach had been employed to prepare several C_1-symmetric *ansa*-metallocenes [6].

As seen in Scheme 1, changes in the bridging unit are limited to substitution on the bridgehead carbon atom. In order to replace the bridging atom itself, an alternate synthetic route has been devised as shown in Scheme 2. These silylene-bridged fluorenyl-containing ligands can function as potential precursors leading to silylene-bridged metallocenes with C_{2v}, C_1 or C_s symmetry.

2.1. Reaction of fluorenyllithium and dichlorodimethylsilane

The product of the reaction of fluorenyllithium (FluLi) and dichlorodimethylsilane depends on the ratio of the two reactants, the order of addition, the reaction temperature and the solvent. When the reaction was carried out in diethyl ether under reflux conditions with a 2:1 ratio of FluLi:Me_2SiCl_2, the main product **7** was isolated with a 70.2% yield. However, in an attempt to prepare **3**, using temperature conditions of -78 °C → 25 °C, tetrahydrofuran (THF) + hexane as the solvent and a ratio of reactants FluLi:Me_2SiCl_2 of 1:1.37, the major product was not **3** but rather **7** again. By changing the reaction solvent to neat hexane in a slurry process and using a 1:2 ratio of FluLi:Me_2SiCl_2, however, the desired product **3** was obtained with a 77.3% yield as colorless crystals (see Section 3). The key intermediate **3** was then converted to the corresponding ligands **5** and **6** with good yields by means of nucleophilic substitution with cyclopentadienyllithium (CpLi) and indenyllithium (IndLi) respectively. Hydrolysis of **3** with water in diethyl ether led to the corresponding disiloxane **4**.

When the above reaction was carried out in a solvent mixture of THF and hexane, using a 1:1.2 ratio of FluLi:Me_2SiCl_2 and the reverse order of addition (adding Me_2SiCl_2 to FluLi in THF solution) at room temperature, a very unusual compound, (9-chlorodimethylsilyl)[9-(9′-fluorenyl)dimethylsilyl]fluorene (**8**), was isolated as colorless needle crystals instead of the expected **3**. A possible mechanism of the reaction is presented in Scheme 3.



Scheme 2.

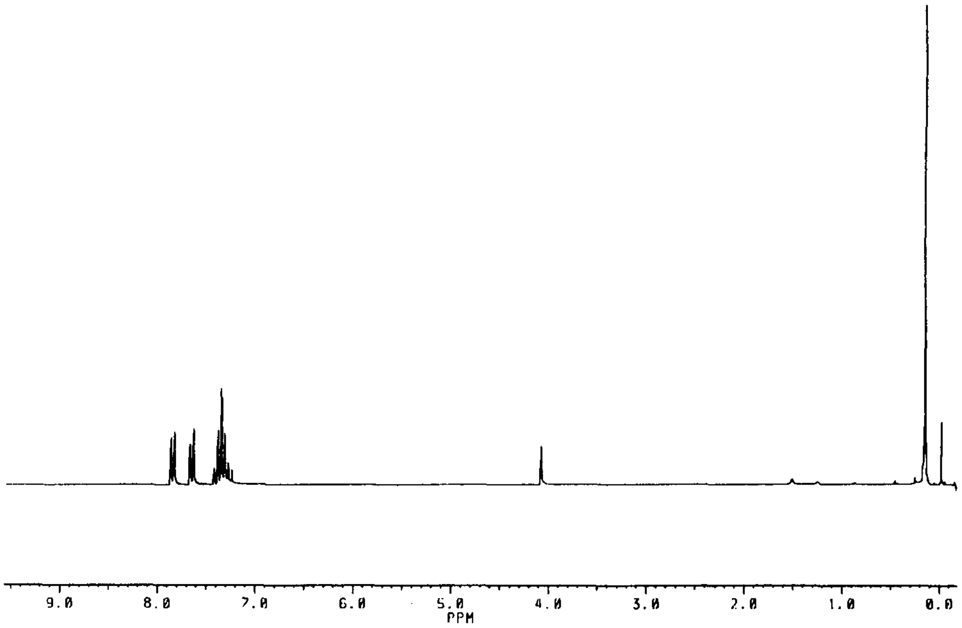


Fig. 1. ^{1}H NMR spectrum of **3** in $CDCl_3$.

Compound **3**, which is believed to be formed first, has two reactive sites. Nucleophilic substitution of **3** with FluLi would lead to **7**, which was detected in the mother liquor during the recrystallization process. Alternatively, proton abstraction by the strong base FluLi would lead to an intermediate, which when followed by a coupling reaction with **3** would give the final product **8**. Hydrolysis of **8** produced the corresponding silanol **9** instead of the disiloxane, probably owing to steric reasons. ^{1}H NMR spectra of both **8** and **9** contain two non-equivalent fluorenyl rings and methyl groups. For comparison, ^{1}H NMR spectra of **3** and **8** are shown in Figs. 1 and 2 respectively.

Two of these new ligands, **6** and **5**, were converted to

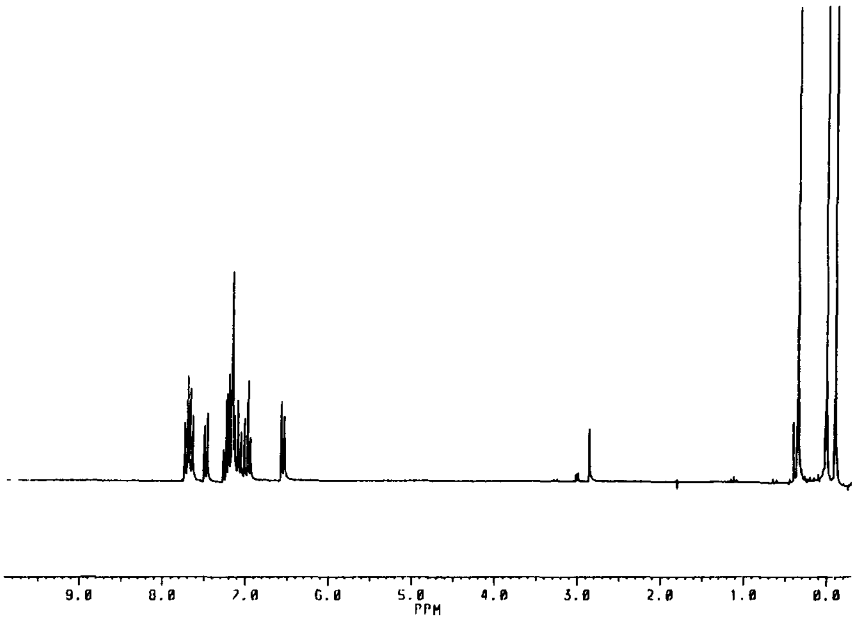


Fig. 2. ^{1}H NMR spectrum of **8** in C_6D_6.

Table 1
Ethylene and propylene polymerizations catalyzed with **1**–MAO [a]

Run	Monomer	[Zr] (μM)	[MAO] (mM)	Time (min)	Yield (g)	$A \times 10^{-6}$ (g polymer (mol Zr)$^{-1}$ [monomer]$^{-1}$ h^{-1})	T_m (°C)	MW [b] $\times 10^{-5}$
1	C_2H_4	10	60	30	0.27	4.77	137	1.06
2	C_3H_6	100	100	60	1.23	0.96	86	2.74

[a] Conditions: toluene, 50 ml; $T_p = 50$ °C; $P(C_2H_4) = P(C_3H_6) = 10$ lbf in^{-2}.
[b] MW by viscosity.

the corresponding zirconium complexes, **1** and **2**, respectively, using well-established methods (see Section 3).

2.2. Polymerization behavior of *1*

Ethylene and propylene were polymerized with **1** activated with MAO; the results are presented in Table 1. The propylene polymerization activity A_p at 50 °C is about 10^6 g PP (mol Zr)$^{-1}$[C_3H_6]$^{-1}$ h^{-1} to produce a polymer having a melting temperature T_m = 86 °C and a high MW of 10^5. The PP has a low tacticity with the methyl pentad distributions (Fig. 3) $[mmmm] = 0.57_5$, $[mmmr] = 0.12_7$, $[rmmr] = 0.02_3$, $[mmrr] = 0.12_9$, $[mrmm] + [rmrr] = 0.03_9$, $[mrmr] = 0.02_4$, $[rrrr] = 0.01_9$, $[mrrr] = 0.03_0$ and $[mrrm] = 0.04_1$, and the triad distributions $[mm] = 0.72_5$, $[mr] = 0.18_4$ and $[rr] = 0.09_0$. Methyl triad mechanistic model tests [2d] of the ^{13}C NMR spectrum indicated an enantiomorphic-site control propagation model associated with an asymmetric metal center.

Previously we have reported the propylene polymerization behaviors of several C_1-symmetric titanocenes activated with MAO [6–8]. They all have a slightly lower A_p of 3×10^5 g PP (mol Zr)$^{-1}$[C_3H_6]$^{-1}$ h^{-1}. More importantly, they produced PP having very different microstructures. The *syn* [7] and *anti* [6a,b] compounds of *rac*-ethylidene-(η^5-tetramethylcyclopentadienyl)(η^5-indenyl)titanium dichloride (**10a**) and dimethyl derivative (**10b**) gave stereoblock homopoly(propylene), comprised of alternating sequences of stereoregular crystalline and stereoirregular amorphous segments which exhibits T_m = 60 °C and excellent mechanical and elastic properties [6a,8]. The corresponding zirconium analog **11** exhibits a very low activity to produce hemi-isotactic PP even though its X-ray molecular structure is not distinguishable from that of the titanocene derivative **10b** [6e]. In the case of racemic compounds isopropylidene-(η^5-cyclopentadienyl)(η^5-indenyl)metal dichlorides (M = Ti (**12a**) or Zr (**12b**)) and the (1-η^5-3-methylindenyl) derivatives (M = Ti (**13a**) or Zr (**13b**)), it is the Zr precursors **12b** and **13b** that polymerize propylene to the hemiisotactic product with $A_p \approx 3 \times 10^5$ g PP (mol Zr)$^{-1}$[C_3H_6]$^{-1}$ h^{-1}, whereas

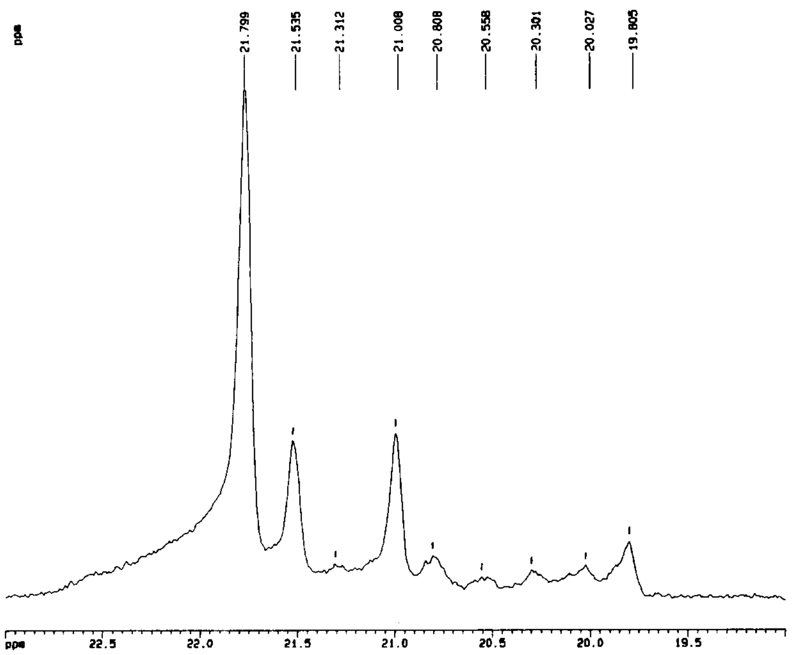
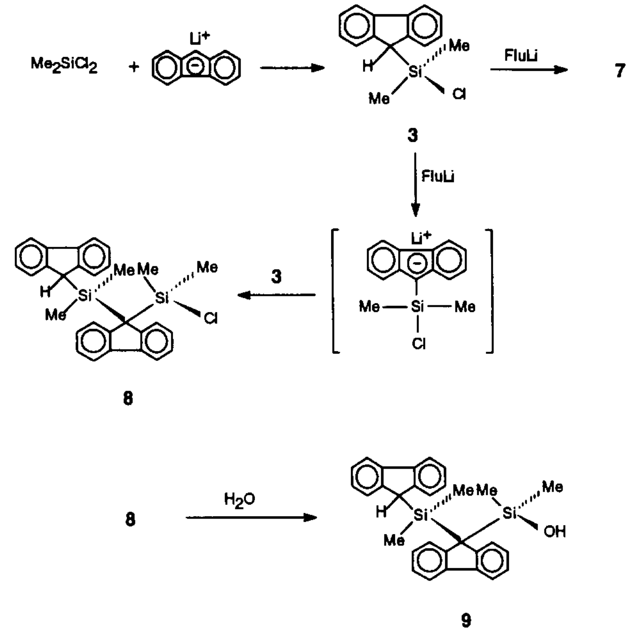


Fig. 3. ^{13}C NMR spectrum of the methyl pentad region of PP obtained with **1**–MAO at T_p = 50 °C.



Scheme 3.

the titanocene compounds **12a** and **12b** are without propylene polymerization activity [6d]. A better understanding of these catalytic differences in spite of their apparent structural similarity merits further investigation.

On the contrary, asymmetric *ansa*-zirconocene complexes with additional stereogenic units can catalyze stereoregular α-olefin polymerization [9]. The formation of *i*-PP with the asymmetric zirconocene precursor **1**, instead of the other types of PP, may indicate that the interconversion of the two catalytic states favors the stereoselective state over the non-stereoselective state in the two-state catalyzed polymerization mechanism for asymmetric catalytic species [6].

2.3. Polymerization behavior of 2

For decades *s*-PP was obtainable only using vanadium coumpounds activated with AlR_2Cl at $T_p < -48$ °C and with low yields. It was an important discovery of Ewen et al. [3a] that isopropylidene-(η^5-cyclopentadienyl) (η^5-fluorenyl)zirconium dichloride (**14**) activated with MAO polymerizes *s*-PP with a high activity at useful T_p. The mechanism of propagation is primary insertion with enantiomorphic-site control as a contrast to secondary insertion with chain-end control for the vanadium catalysts. Ewen et al. [10] proposed that migratory insertion to a C_s-symmetric metal–carbon σ bond leads naturally to syndiotactic placement and that site isomerization without insertion introduces an isotactic defect. We have recently synthesized the *rac*-2,2-dimethylpropylidene-(η^5-cyclopentadienyl)(η^5-fluorenyl)-zirconium dichloride (**15**) [3c] which has an asymmetric carbon atom bridge. The catalyst system **15**–MAO is just as active as **14**–MAO and is even more syndioselective in comparison. Therefore, if C_s symmetry is required for syndiospecific catalysis, then it is the local symmetry and not the global molecular symmetry which is the determinant factor.

The new precursor **2** was activated with MAO; the results of ethylene polymerization (runs 3 and 4) and propylene polymerization (runs 5–7) are summarized in Table 2. $A_p \approx 10^7$ g PP (mol Zr)$^{-1}$ [C_3H_6]$^{-1}$ h^{-1} at 25 °C, and it is twice this value at 50 °C. This result is compared with $A_p = 2 \times 10^6$ and 10^6 at 30 °C for **15**–MAO and **14**–MAO respectively.

Unfortunately, **2**–MAO produced *a*-PP rather than the expected *s*-PP. The sample from run 6 was analyzed with ^{13}C NMR spectroscopy to have the triad distributions $[mm] = 0.35_1$, $[mr] = 0.52_3$ and $[rr] = 0.12_6$. Previously, Ewen et al. [10b] have reported low syndioselectivities for some C_s-symmetric zirconocene catalysts. For instance, isopropylidene-(cyclopentadienyl) (4,5-methylenephenanthrenyl)zirconium dichloride (**16**), dimethylsilylene-(cyclopentadienyl)(4,5-methylenephenanthrenyl)zirconium dichloride (**17**), and dimethylsilylene(cyclopentadienyl)(tetramethylcyclopentadienyl)zirconium dichloride (**18**) produced polypropylene having $[rrrr]$ populations of 0.72, 0.24 and 0.14 respectively. As shown from the above examples, replacement of the carbon bridge with a Si bridge results in a large drop in syndiotacticity, which contrasts sharply with the isospecific cases [4b,5]. Ewen [10b] attributed the differences in his studies to the metal–centroid angles which

Table 2
Ethylene and propylene polymerizations catalyzed with **2**–MAO [a]

Run	Monomer	T_p (°C)	[Zr] (μM)	[MAO] (mM)	Time (min)	Yield (g)	$A \times 10^{-6}$ (g polymer (mol Zr)$^{-1}$ [monomer]$^{-1}$ h^{-1})	T_m (°C)	MW [b] $\times 10^{-4}$
3	C_2H_4	0	10	70	5	0.43	28.8	141	32.1
4	C_2H_4	50	10	60	2	0.72	191	139	15.7
5	C_3H_6	0	25	75	25	3.79	9.73	–	14.0
6	C_3H_6	25	25	60	25	3.57	13.6	–	4.58
7	C_3H_6	50	25	50	25	3.07	23.0	–	2.61

[a] Conditions: toluene, 50 ml; $P(C_2H_4) = P(C_3H_6) = 10$ lbf in^{-2}.
[b] MW by viscosity.

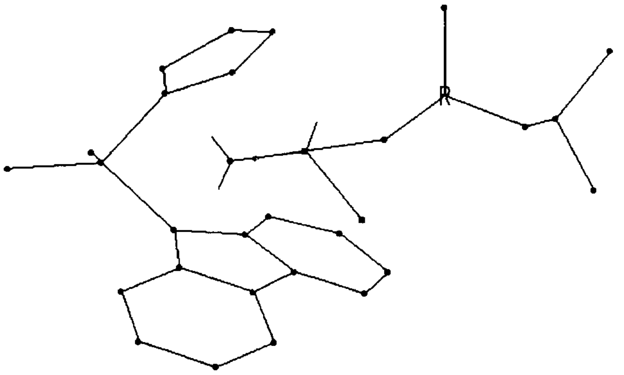


Fig. 4. Calculated structure for the third insertion of $Me_2Si(Flu)(Cp)Zr^+(R\text{-}C_7H_{15})$ (re-C_3H_6) π complex.

are 117.9° in **16** and 128.1° in **17**. It was rationalized that the 10.2° larger angle and thus less steric hindrance are responsible for the inferior π-face selectivity of the latter than the former catalyst system for a chain-end controlled propagation.

We investigated further the lack of syndioselectivity for **2** with the aid of molecular mechanics calculations performed on the π complexes using the geometry of these intermediates obtained by ab-initio calculations [11]. The optimized structures for the third insertion of propylene for racemic enchainment and meso enchainment are shown in Figs. 4 and 5 respectively. The methyl group of the π-complexed propylene with *re* face is directed toward the space between the two six-membered rings of the fluorenyl ligand for the polymer chain with the β-carbon atoms having either the *R* or the *S* configuration (Fig. 4). On the contrary, the structure with the *si* face of propylene complexed suffers non-bonded interaction between its methyl group and that of the β-carbon atom (Fig. 5), which has a higher steric energy. Therefore the absence of syndioselectivity is attributable to the fact that its enantiofacial selection for the *re* olefin is always preferred over the *si* face. On the contrary, in the case of **14**, the calculation showed [3c] that complexing of the *re* face of propylene is favored with the β-carbon atom having an *R* configuration, whereas the *si* face is favored with an *S* configuration of the β-carbon atom, thus resulting in a syndiotactic polymer chain.

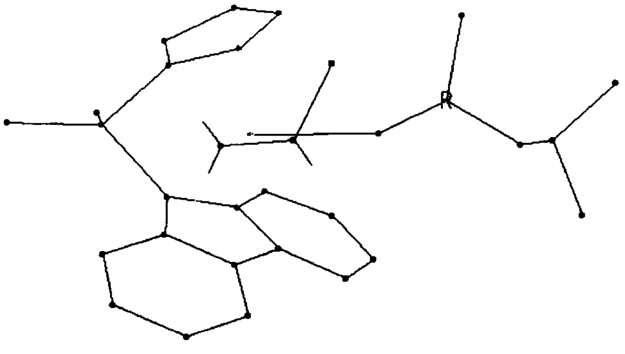


Fig. 5. Calculated structure for the third insertion of $Me_2Si(Flu)(Cp)Zr^+(R\text{-}C_7H_{15})$ (si-C_3H_6) π complex.

The ethylene polymerization activity of **2**–MAO is 40 times greater than that of **1**–MAO at 50 °C, whereas the difference in A_p is about twentyfold, also in favor of the former. On the contrary, the MW of PP given by the former is much lower than the MW of the latter. Compared with *rac*-$Me_2Si(Ind)_2ZrCl_2$ (**19**)–MAO [5e] that we reported previously, **1**–MAO exhibits much lower activities for both ethylene and propylene polymerizations but higher MWs of products, whereas the **2**–MAO catalyst system gives similar polymerization results in terms of A and MW. From the observed catalytic behaviors discussed above, one may conclude that steric factors have a strong influence on polymerization activity, whereas the electronics contribution dominates polymer MW control, assuming that the electron-donating ability decreases in the order Flu > Ind > Cp. Higher electron density at the metal center tends to stabilize the olefin π complex to weaken the metal–carbon σ bond and to reduce the affinity for β-hydride elimination, resulting in a higher MW of polymer.

In conclusion, we have demonstrated a convenient synthetic route leading to silylene-bridged fluorenyl-containing ligands and synthesized seven new ligands using this method. Two newly synthesized zirconocene precursors derived from those ligands catalyzed ethylene and propylene polymerizations with different activities and stereochemistry. The stereochemistry and activity of olefin polymerization by C_1 or C_s symmetric metallocenes are less predictable than the isospecific C_2 symmetric metallocenes. Comparisons with the polymerization behaviors of other C_1 and C_s symmetric metallocenes showed no necessary correlation of symmetry and molecular structure of metallocene precursor with activity and stereoselectivity of olefin polymerization.

3. Experimental section

All reactions were carried out using Schlenk or glove-box techniques under an argon atmosphere. Solvents were dried over Na–K alloy or CaH_2 (CH_2Cl_2) and distilled under argon prior to use. Routine ^1H NMR spectra were recorded on a Bruker AC-200 spectrometer at ambient temperature; chemical shifts are referenced with respect to tetramethylsilane. ^{13}C NMR spectra of the polymer products were measured on a Bruker AMX-500 spectrometer (125.77 MHz) in $C_2D_2Cl_4$ at 110 °C. Elemental analyses were performed by the Microanalytical Laboratory at the University of Massachusetts, Amherst. Melting points were uncorrected.

CpLi, IndLi and FluLi were prepared from reaction of the corresponding hydrocarbons and *n*-BuLi in THF.

After removal of the solvent, the residues were washed with hexane and dried in vacuo to give the lithium salts in quantitative yields. MAO was obtained from Akzo Chemicals. Ethylene and propylene were purchased from Mariam Graves and purified by passing through two Matheson gas purifiers (model 6404). Unless otherwise indicated, all other chemicals were obtained from Aldrich.

Polymerizations were carried out in a 250 ml crown-capped glass pressure reactor with a magnetic stirring bar. The system was first evacuated and flushed with argon; then 50 ml of toluene were injected. The system was evacuated again and saturated with the appropriate monomer for about 20 min. The order of addition of reagents and detailed procedures for polymerizations have been described previously [4,12]. The polymerization mixture was quenched with acidic methanol (containing 1% HCl), filtered, washed with methanol and dried at 70 °C to a constant weight.

The values of the activity *A* were calculated using the measured solubility of propylene and ethylene [13]. The intrinsic viscosities of polyethylene and PP were measured in decalin at 135 °C using an Ubbelohde viscometer, and the melting temperatures were measured by differential scanning calorimetry (Perkin-Elmer DSC 4). Stereo-regularities and regioregularities of the polymers obtained were determined by ^{13}C NMR spectroscopy and analyzed by known methods [2d,12a,14].

Molecular mechanics calculations were performed with Allinger's MM2 [15] program and details of the modeling have been described earlier [3c,11,16]. All calculations were carried out using the CAChe Modeling Software system (3.6 version, 1994).

3.1. *Chlorodimethyl-(9-fluorenyl)silane (3)*

Into a 1000 ml Schlenk flask was placed a solution of dichlorodimethylsilane (15.0 ml, 124 mmol) in 200 ml of hexane and the solution was pre-cooled to −78 °C. A suspension of fluorenyllithium (10.3 g, 60.0 mmol) in 500 ml of hexane was slowly added via a cannula and the reaction mixture was stirred for an additional 1 h at this temperature. The resulting mixture was gradually allowed to warm to room temperature and stirred for another 2 h. The reaction mixture was then filtered through a Celite plug. The filtrate was concentrated and kept at −20 °C overnight. The resulting faint-yellow crystals were recrystallized from hexane at −20 °C to afford 12.0 g (77.3% yield) of **3** as colorless crystals (melting point (m.p.), 96.0–97.0 °C). Anal. Found: C, 69.18; H, 5.83. $C_{15}H_{15}ClSi$ Calc.: C, 69.61; H, 5.84%. ^{1}H NMR ($CDCl_3$): δ 7.86 (d, $J = 8.00$ Hz, 2H, arom. H), 7.66 (d, $J = 8.00$ Hz, 2H, arom. H), 7.40 (t, $J = 6.00$ Hz, 2H, arom. H), 7.33 (t, $J = 6.00$ Hz, 2H, arom. H), 4.09 (s, 1H, H-9 Flu), 0.17 (s, 6H, CH_3) ppm. ^{1}H NMR (C_6D_6): δ 7.69 (d, 2H, arom. H), 7.56 (d, 2H, arom. H), 7.28–7.16 (m, 4H, arom. H), 3.77 (s, 1H, 9-H Flu), −0.07 (s, 6H, CH_3) ppm.

3.2. *Bis(9-fluorenyl)tetramethyldisiloxane (4)*

Compound **3** (2.10 g, 8.11 mmol) was reacted with 5 ml of water in 50 ml of diethyl ether with stirring for 30 min. The mixture was then poured into a separatory funnel, and the organic layer was separated and saved. The aqueous layer was extracted twice with diethyl ether, and the combined organic portions were dried over anhydrous magnesium sulfate. The drying agent was filtered, and the solvent of the filtrate was removed. The resulting white solid was recrystallized from diethyl ether and hexane to afford 1.55 g (82.7%) of **4** as colorless cystals (m.p., 212–213 °C). Anal. Found: C, 77.75; H, 6.57. $C_{30}H_{30}OSi_2$ Calc.: C, 77.87; H, 6.53%. ^{1}H NMR ($CDCl_3$): δ 7.82 (d, $J = 8.00$ Hz, 4H, arom. H), 7.37–7.25 (m, 12H, arom. H), 3.75 (s, 2H, 9-H Flu), −0.16 (s, 12H, CH_3) ppm.

3.3. *(Cyclopentadienyl)(9-fluorenyl)dimethylsilane (5)*

A THF solution of cyclopentadienyllithium (15.5 mmol) was added dropwise at room temperature to the flask containing **3** (3.88 g, 15.0 mmol) in 50 ml of THF. After the addition was complete, the reaction mixture was stirred for an additional 4 h. The solvent was removed under vacuum, and the residue was treated with 150 ml of hexane. The suspension was filtered through Celite, and the solvent of the filtrate was removed. The crude product was purified by passage through a silica gel column (200–400 mesh, 1 : 1 methylene chloride : hexane as an elution solvent) to afford 3.06 g (70.7%) of **5** as a yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.94 (d, $J = 8.30$ Hz, 2H, arom. H, Flu), 7.61 (d, $J = 8.30$ Hz, 2H, arom. H, Flu), 7.49–7.32 (m, 4H, arom. H, Flu), 6.61 (m), 6.22 (m) (4H, vinyl H, Cp), 4.02 (s, 1H, H-9, Flu), 3.27 (br.s), 2.80 (s) (1H, CH, Cp), −0.16 (s, 6H, 2 CH_3) ppm.

3.4. *(9-Fluorenyl)(1-indenyl)dimethylsilane (6)*

A 250 ml three-necked flask was equipped with a reflux condenser, magnetic stirring bar and dropping funnel. Indenyllithium (2.50 g, 20.5 mmol) was added to the flask followed by 100 ml of diethyl ether. Stirring was begun and **3** (4.92 g, 19.0 mmol) in 100 ml of diethyl ether was added dropwise at room temperature. After the addition was complete, the reaction mixture was heated at reflux with stirring for 6 h. The resulting reaction mixture was hydrolyzed with water and extracted with diethyl ether. The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to provide the crude product as a yellow solid. Recrystallization from diethyl ether and hexane at −20 °C gave 5.22 g (81.2%) of **6** as faint-yellow crystals (m.p., 108–109 °C). Anal. Found: C, 85.08; H, 6.55. $C_{24}H_{22}Si$ Calc.: C, 85.15; H, 6.55%. ^1H NMR (C_6D_6): δ 7.78 (d, $J = 8.00$ Hz, 2H, arom. H), 7.44–7.10 (m. 10H, arom. H), 6.79 (dd, $J_{ab} = 5.37$ Hz, $J_{ax} = 1.96$ Hz, 1H, H-3 Ind), 6.25 (dd, $J_{ba} = 5.37$ Hz, $J_{bx} = 1.96$ Hz, 1H, H-2 Ind), 3.89 (s, 1H, 9-H Flu), 3.63 (s, 1H, H-1 Ind), −0.36 (s, 3H, CH_3), −0.56 (s, 3H, CH_3) ppm.

3.5. *Bis(9-fluorenyl)dimethylsilane (7)*

A 500 ml round-bottom flask was equipped with a reflux condenser, a magnetic stirring bar and dropping funnel. Fluorenyllithium (5.00 g, 29.0 mmol) was added to the flask followed by 200 ml of diethyl ether. Stirring was begun and dichlorodimethylsilane (14.5 mmol) in 100 ml of diethyl ether was added dropwise at room temperature. After the addition was complete, the reaction mixture was heated at reflux with stirring for 6 h. The resulting reaction mixture was hydrolyzed with ice water and extracted twice with diethyl ether. The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to provide the crude product as a faint-yellow solid. Recrystallization from diethyl ether at −20 °C gave 3.95 g (70.2% yield) of **7** as colorless needle crystals (m.p., 182–183 °C ([17] 178–179 °C, 3% yield)). Anal. Found: C, 86.53; H, 6.21. $C_{28}H_{24}Si$ Calc.: C, 86.55; H, 6.23%. ^1H NMR ($CDCl_3$): δ 7.90 (d, $J = 8.00$ Hz, 4H, arom. H), 7.54 (d, $J = 8.00$ Hz, 4H, arom. H), 7.36 (t, $J = 6.00$ Hz, 4H, arom. H), 7.30 (t, $J = 6.00$ Hz, 4H arom. H), 4.27 (s, 2H, H-9), −0.19 (s, 6H, CH_3) ppm. ^1H NMR (C_6D_6): δ 7.79 (d, 4H, arom. H), 7.39 (d, 4H, arom. H), 7.28–7.16 (m, 8H, arom. H), 4.20 (s, 2H, H-9 Flu), −0.58 (s, 6H, CH_3) ppm.

3.6. *(9-Chlorodimethylsilyl)[9-(9′-fluorenyl)dimethylsilyl]fluorene (8)*

Into a 250 ml Schlenk flask equipped with an addition funnel was placed fluorene (10.0 g, 60.2 mmol) and 50 ml of THF. *n*-BuLi (37.6 ml, 1.6 M in hexane, 60.2 mmol) was added dropwise at room temperature. The resulting deep-red solution was stirred for several hours until gas evolution had completely ceased, and a solution of 8.77 ml (72.3 mmol) of dichlorodimethylsilane in hexane (60 ml) was added. The reaction mixture was stirred overnight and a yellow suspension was obtained. The mixture was filtered and the solvent as well as unreacted $(CH_3)_2SiCl_2$ were removed under vacuum. The solid was recrystallized from diethyl ether at −20 °C to afford 2.69 g (18.6% yield) of **8** as colorless needle crystals (m.p., 208–209 °C). Anal. Found: C, 75.19; H, 6.04. $C_{30}H_{29}ClSi_2$ Calc.: C, 74.88; H, 6.07%. ^1H NMR ($CDCl_3$): δ 7.87 (d, $J = 8.00$ Hz, 2H, arom. H), 7.76 (d, $J = 8.00$ Hz, 2H, arom. H), 7.52–7.35 (m, 6H, arom. H), 7.10 (t, $J = 6.00$ Hz, 2H, arom. H), 6.91 (t, $J = 6.00$ Hz, 2H, arom. H), 6.40 (d, $J = 8.00$ Hz, 2H, arom. H), 2.77 (s, 1H, H-9 Flu), 0.36 (s, 6H, CH_3), 0.04 (s, 6H, CH_3) ppm. ^1H NMR (C_6D_6): δ 7.68 (dd, 4H, arom. H), 7.47 (d, 2H, arom. H), 7.23–7.00 (m, 8H, arom. H), 6.56 (d, 2H, arom. H), 2.85 (s, 1H, H-9 Flu), 0.34 (s, 6H, CH_3), −0.11 (s, 6H, CH_3) ppm.

3.7. *(9-Dimethylsilanol)[9-(9′-fluorenyl)dimethylsilyl]fluorene (9)*

Compound **8** (1.00 g, 2.08 mmol) was reacted with 10 ml of water in 100 ml of diethyl ether with stirring for 1 h. The reaction mixture was then poured into a separatory funnel and the organic layer was separated and saved. The aqueous layer was extracted with diethyl ether twice and the combined organic portions were dried over anhydrous magnesium sulfate. The drying agent was filtered, and the solvent of the filtrate was removed. The resulting white solid was recrystallized from diethyl ether to afford 0.75 g (77.9%) of **9** as colorless crystals (m.p., 131 °C). Anal. Found: C, 78.12; H, 6.58. $C_{30}H_{30}OSi_2$ Calc:. C, 77.87; H, 6.53%. ^1H NMR ($CDCl_3$): δ 7.90 (d, $J = 8.00$ Hz, 2H, arom. H), 7.63 (d, $J = 8.00$ Hz, 2H, arom. H), 7.55 (d,$J = 8.00$ Hz, 2H, arom. H), 7.39–7.32 (m, 4H, arom. H), 7.12 (t, $J = 6.00$ Hz, 2H, arom. H), 6.93 (t, $J = 6.00$ Hz, 2H, arom. H), 6.45 (d, $J = 8.00$ Hz, 2H, arom. H), 2.82 (s, 1H, H-9 Flu), 1.70 (s, 1H, OH), 0.30 (s, 6H, CH_3), −0.20 (s, 6H, CH_3) ppm.

3.8. *Dimethylsilylene-(η^5-indenyl)(η^5-fluorenyl)zirconium dichloride (1)*

To a solution of **6** (1.31 g, 3.86 mmol) in 30 ml of THF, two equivalents of methyllithium in diethyl ether were added dropwise at room temperature. The resulting red solution was stirred for an additional 4 h, the solvents then removed under vacuum, and the residue dried under high vacuum overnight. The solid was washed with pentane to give the dilithiated compound as an orange powder with a quantitative yield. The powder was used for the next reaction without further purification.

The above dry dilithium salt was mixed with $ZrCl_4$ (0.90 g, 3.86 mmol) followed by the addition of 50 ml of dry pentane. The resulting suspension was stirred at room temperature overnight, the pentane was decanted, and the remaining solid was extracted with methylene chloride. The resulting red suspension was filtered through a Celite plug to remove LiCl. Cooling the filtrate at −20 °C for 1 week gave 0.35 g (18.2% ([18] 20%)) of **1** as a red crystalline solid.

3.9. Dimethylsilylene-(η^5-cyclopentadienyl)(η^5-fluorenyl)zirconium dichloride (2)

Compound **5**, methyllithium and $ZrCl_4$ were treated as described for the synthesis of the compound **1**, affording **2** (4.5%) as orange crystals. Anal. Found: C, 53.06; H, 3.91. $C_{20}H_{18}Cl_2SiZr$ Calc: C, 53.55; H, 4.04%. ^1H NMR (CD_2Cl_2): δ 7.69 (d, $J = 6.86$, 2H, Flu), 7.28–7.18 (m, 6H, Flu), 6.43 (m, 2H, Cp), 6.07 (m, 2H, Cp), 0.37 (s, 6H, CH_3) ppm.

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