A Silylene-Bridged (Isodicyclopentadienyl)(Fluorenyl) Complex of Zirconium for Homogeneous Olefin Polymerization

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The synthesis and characterization of the new silylene(isodicyclopentadienyl)(fluorenyl)-zirconium dichloride (**5**) have been performed. This complex has been characterized by ^{1}H and ^{13}C NMR spectroscopy and its solid-state molecular structure has been determined. After activation by methylalumoxane, **5** is shown to initiate the polymerization of ethylene and propylene. S-PP is produced. Quite unusual for a silylene-bridged zirconium complex, good syndiotacticity was observed for propylene polymerization.

Introduction

The catalytic behavior of homogeneous group 4 metallocene/methylalumoxane Ziegler catalysts for olefin polymerization has been actively investigated for several decades. Such metallocene complexes have potential for the access to polyolefins with various compositions and microstructures. In the case of propylene polymerization, group 4 *ansa*-metallocene catalysts lead to the formation of highly isotactic polypropylene when a C_2 symmetric complex is involved. Slight variations in the catalyst structure have consequences on the stereospecificity of polymer produced, and atactic polypropylene is obtained. Moreover, syndiospecific propylene polymerization was discovered by Ewen et al.[1] with C_s symmetrical isopropylidene(cyclopentadienyl)(fluorenyl)zirconium dichloride (**1**). Syndiotactic polypropylene growing chains are thus generated in the presence of such fluorenyl complexes from the alternating linking of inverse relative configuration monomer units during the catalyst site isomerization. Although modifications of the carbon linker methyl groups by phenyl groups as in **2**[2,3] did not modify the polymer stereoregularity, replacement of the isopropylidene bridge by a silylene one as in **3** produced atactic polypropylene[4] due to the larger centroid−metal−centroid bite angle.[4,5] In addition, Bercaw[6,7] showed that doubly bridged *ansa*-metallocenes such as **4** with typical C_s symmetry and a bulky ligand like the fluorenyl ligand can result in the formation of highly syndiotactic polypropylene. It has been assumed that even with a large centroid−metal−centroid angle, syndiospecificity can be realized when complexes contain a cyclopentadienyl ligand bulky enough to force the orientation of the methyl group of the incoming monomer unit to the open region of the flat fluorenyl ligand. Our investigations involving isodicyclopentadienyl ligand utilization for the synthesis of group 4 metallocene[8−13] complexes allowed us to anticipate that the presence of fluorenyl and isodicyclopentadienyl ligands in the same complex could lead to syndiotactic polypropylene when activated with MAO. We report below the synthesis, characterization, and polymerization behavior of complex **5**, the first isodicyclopentadienyl-bridged complex. To the best of our knowledge, few examples of dimethylsilylene cyclopentadienyl ligands−fluorenyl zirconium complexes are described in the literature[4,14−16] and from among them

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(1) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. *J. Am. Chem. Soc.* **1988**, *110*, 6255−6256.

(2) Alt, H. G.; Milius, W.; Palackal, S. J. *J. Organomet. Chem.* **1994**, *472*, 113−118.

(3) Razavi, A.; Atwood, J. L. *J. Organomet. Chem.* **1993**, *459*, 117−123.

(4) Chen, Y.-X.; Rausch, M. D.; Chien, J. C. W. *J. Organomet. Chem.* **1995**, *497*, 1−9.

(5) Resconi, L.; Jones, R. L.; Rheingold, A.; Yap, G. P. A. *Organometallics* **1996**, *15*, 998−1005.

(6) Herzog, T. A.; Zubris, D. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 11988−11989.

(7) Miyake, S.; Bercaw, J. E. *J. Mol. Catal. A: Chem.* **1998**, *128*, 29−39.

(8) Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Crocq, V. *Organometallics* **1988**, *7*, 1873−1875.

(9) Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Sornay, C.; Rogers, R. D.; Rheingold, A. *Organometallics* **1989**, *8*, 2159−2167.

(10) Sornay, C.; Meunier, P.; Gautheron, B.; O'Doherty, G. A.; Paquette, L. A. *Organometallics* **1991**, *10*, 2082−2083.

(11) Zaegel, F.; Gallucci, J. C.; Meunier, P.; Gautheron, B.; Bzowej, E. I.; Paquette, L. A. *Organometallics* **1995**, *14*, 4576−4584.

(12) Gobley, O.; Meunier, P.; Gautheron, B.; Gallucci, J. C.; Erker, G.; Dahlmann, M.; Schloss, J. D.; Paquette, L. A. *Organometallics* **1998**, *17*, 4897−4903.

(13) Gentil, S.; Pirio, N.; Meunier, P.; Gallucci, J. C.; Schloss, J. D.; Paquette, L. A. *Organometallics* **2000**, *19*, 4169−4172.

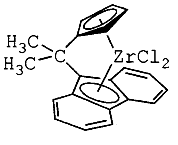
(14) Obora, Y.; Stern, C. L.; Marks, T. J.; Nickias, P. N. *Organometallics* **1997**, *16*, 2503−2505.

(15) Thomas, E. J. *J. Organomet. Chem.* **2001**, *631*, 29−35.

(16) Fan, W.; Leclerc, M. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 9555−9563.

10.1021/om020384x CCC: $22.00

X-ray structures are reported for only three dichloro complexes.[5,14,17]



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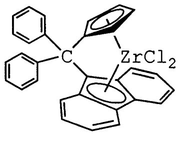

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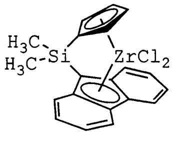

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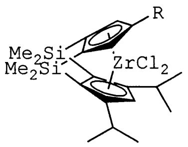

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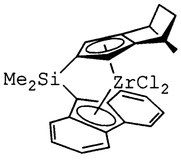

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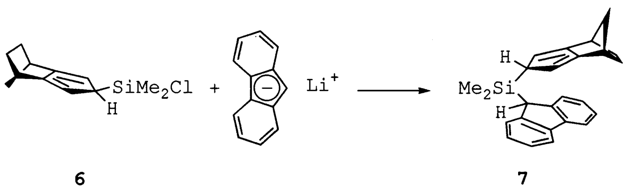
Results and Discussion

The approach employed to synthesize the C_s symmetrical complex **5** consists of the traditional synthetic route for silylene-bridged *ansa*-metallocene complexes. Chen et al.[4] described the synthesis of dimethylsilylene(cyclopentadienyl)(fluorenyl)zirconium dichloride by reaction of cyclopentadienyllithium with chlorodimethyl(9-fluorenyl)silane, followed by $ZrCl_4$ addition. Chlorodimethyl(9-fluorenyl)silane formation is obtained by reaction of fluorenyllithium with dichlorodimethylsilane in a process that is highly dependent on the ratio of the two reactants.[4] In all cases, at least 10% of bis(9-fluorenyl)dimethylsilane is formed.[4,18] In this work (Scheme 1), formation of the bis-fluorenyl derivative was limited by prior preparation of chlorodimethyl(isodicyclopentadienyl)silane **6** as described in a previously reported work.[13] Reaction of **6** at −78 °C with fluorenyllithium in diethyl ether led to the complex precursor (isodicyclopentadienyl)(9-fluorenyl)dimethylsilane (**7**).

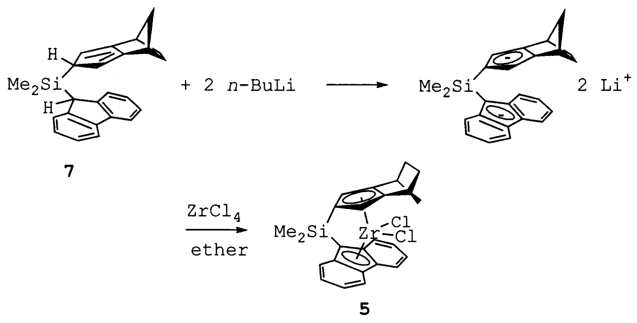
Double deprotonation of **7** with 2 equiv of *n*-butyllithium and subsequent reaction of the dilithium salt with $ZrCl_4$ in diethyl ether (Scheme 2) afforded uniquely the dichloro zirconocene complex **5**. Dissolution of **5** in toluene and recrystallization afforded single crystals suitable for X-ray diffraction. Chemical shift assignments have been made according to the ^1H NMR (Figure 1) and ^{13}C NMR correlated spectroscopy in line with prior results in the isodicyclopentadiene field.[9,10] It appeared that the isodicyclopentadienyl ligand was evidently complexed on its *exo* face in a completely stereoselective manner.

The characteristic signals of the isodicyclopentadienyl ligand can be easily detected. Its peripheral 11 and bridgehead 12 protons appear at δ 5.15 and 3.23 ppm, respectively. The methano 14 and ethano 13 bridge protons give rise to two sets of double multiplets between 1.01 and 2.51 ppm. The *syn*-methano bridge proton chemical shift at 2.51 ppm is observed to be 0.5 ppm more shielded than in classical nonbridged isodicyclopentadienyl complexes.[9−12] The corresponding chemicals shifts of the fluorenyl ligand protons are within the range of δ 7.23−8.23 ppm and appear as two sets of double triplets centered at δ 7.45 and 8.03 ppm and two sets of triple multiplets at 7.23 and 7.59 ppm.

Scheme 1



Scheme 2



Crystal Structure Results. The molecular structure of **5** is illustrated in Figure 2, with relevant bond lengths and angles listed in Table 1. As expected, replacement of an isopropylidene bridge by a silylene one results in increasing the centroid−metal−centroid angle. The Cp(1)−Zr−Cp(2) angle is 129.12(3)° for complex **5** and 118.6° in the case of complex **1**. Similar centroid−metal−centroid angles of 130.3(1)° and 128.1° are reported for $Me_2Si(Flu)_2ZrMe_2$[5] and dimethylsilylene(cyclopentadienyl)(4,5-methylene-phenanthrenyl)zirconium dichloride,[4] respectively. No steric consequences from the silylene bridge are noted compared to unbridged isodicyclopentadienyl complexes. The angles about the metal atom are in the same range in the silylene-bridged complex **5** as in the nonbridged isodicyclopentadienyl zirconium dichloro derivatives.[9,12,19] As observed in all isodicyclopentadienyl molecular structures, the norbornane fragment is slightly bent to the *endo* side of the ligand. This bending, as defined by the dihedral angle between the least-squares plane C(6)−C(5)−C(1)−C(9) and the plane C(3)−C(2)−C(1)−C(5)−C(4), is 10.2(1)° in **5**. The Cl(1)−Zr−Cl(2) angle is 98.41(1)°. The fluorenyl Zr−C bond distances are similar to metal−carbon bond values described for unbridged Flu_2ZrCl_2.[5,20] The observed progressive increase of the fluorenyl Zr−C bond lengths from C(23) (2.408(2) Å) to C(11,22) (2.556(2) and 2.558(2) Å) and C(16,17) (2.763(2) and 2.763(2) Å) could indicate the presence of a η^3-coordinated system and thus a 14-electron complex.

Olefin Polymerization. When activated with MAO, precursor **5** proved to be active for ethylene and propylene polymerization (Table 2). At 20 °C, under a constant ethylene pressure of 4 bar, **5-**MAO exhibits a polymerization activity of 500 kg of PE/((mol Zr)[*P*, bar]·h). This activity value is seen to be in the good range of results obtained with other fluorenyl ligand complexes. Schmid and Alt[21] reported a 8-fold higher activity (1610 kg of PE/((mol Zr)[*P*, bar]·h) for Flu_2ZrCl_2

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(17) Patsidis, K.; Alt, H. G.; Milius, W.; Palackal, S. J. *J. Organomet. Chem.* **1996**, *509*, 63−71.

(18) Okuda, J.; Schattenmann, J.; Wocadlo, S.; Massa, W. *Organometallics* **1995**, *14*, 789−795.

(19) Gallucci, J. C.; Gautheron, B.; Gugelchuk, M.; Meunier, P.; Paquette, L. A. *Organometallics* **1987**, *6*, 15−19.

(20) Kowala, C.; Wailes, P. C.; Weigold, H.; Wunderlich, J. A. *J. Chem. Soc., Chem. Commun.* **1974**, 993−994.

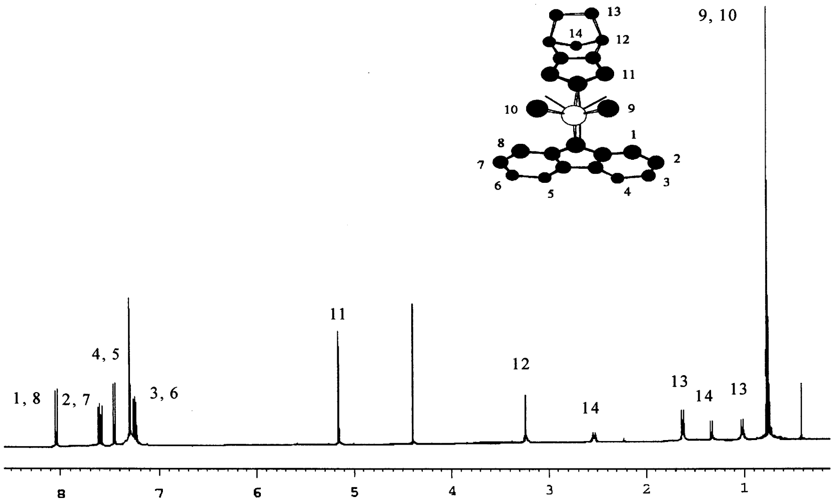

Figure 1. ^{1}H NMR spectrum of **5** in C_6D_6.

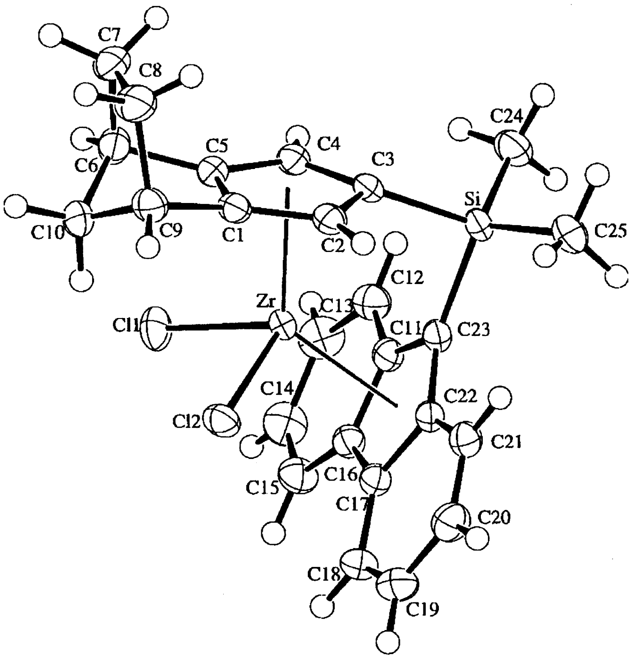

Figure 2. Ortep drawing of the molecular structure of **5**.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for 5[a]

Zr−Cl(l)	2.4260(4)	Zr−Cl(2)	2.4337(4)
Zr−C(l)	2.549(2)	Zr−C(23)	2.408(2)
Zr−C(2)	2.491(2)	Zr−C(11)	2.556(2)
Zr−C(3)	2.473(2)	Zr−C(22)	2.558(2)
Zr−C(4)	2.481(2)	Zr−C(16)	2.763(2)
Zr−C(5)	2.544(2)	Zr−C(17)	2.763(2)
Zr−Cp(l)	2.1974(7)	Zr−Cp(2)	2.3065(7)
Si−C(3)	1.868(2)	Si−C(23)	1.870(2)
Cp(l)−Zr−Cp(2)	129.12(3)	C(3)−Si−C(23)	95.03(7)
Cl(l)−Zr−Cl(2)	98.41(1)	C(25)−Si−C(24)	110.00(9)

[a] Cp(1) and Cp(2) are the ring centroids for C(1), C(2), C(3), C(4), and C(5) of the isodicyclopentadienyl ligand and C(11), C(16), C(17), C(22), and C(23) of the fluorenyl ring, respectively.

at 30 °C with an ethylene pressure of 10 bar, whereas 52 kg of PE/((mol Zr)[*P*, bar]·h) can be calculated under Chen's[4] polymerization conditions (0 °C, 10 bar of ethylene).

Preliminary relative measures of **5**-MAO propylene polymerization efficiency show a quite low activity value of 30 kg of PP/((mol Zr)[*P*, bar]·h) at 20 °C compared with other silylene-bridged fluorenyl complexes. The propylene polymerization activity decreases significantly with an increase of the polymerization temperature. When polymerizations of propene were conducted at 20 °C, a nonsticky material was obtained. In contrast, at 70 °C a sticky solid was produced. ^{13}C NMR sample analysis of the methyl pentad region confirms the production of atactic polypropylene at 70 °C and syndiotactic polypropylene at 20 °C (Table 2).

Conclusion

In summary, the first isodicyclopentadienyl-bridged zirconium complex has been synthesized and characterized in order to expand the isodicyclopentadienyl complex family for olefin polymerization. The above-described complex **5**, when activated with MAO, was found to be efficient for ethylene and propylene polymerization. In the case of propylene, activities were found to be rather low but we have shown that the presence of the *exo*-isodicyclopentadienyl bulky moiety combinated with the fluorenyl one leads to highly syndiotactic polypropylene at 20 °C. So, to test the ability of isodicyclopentadienyl ligand to induce a high tacticity of polymers in polymerization catalysis other bridged complexes are currently being investigated.

Experimental Section

General Conditions. All manipulations were conducted under an argon atmosphere. The solvents were dried and distilled prior to use. Butyllithium, fluorene, and $ZrCl_4$ were obtained from Aldrich and used as received. Ethylene (N35) and propylene (N24) were purchased from Air Liquide and MAO (10 wt %) from Crompton. Fluorenyllithium was prepared from fluorene and *n*-BuLi in diethyl ether. Chlorodimethyl(9-fluorenyl)silane,[4,5] isodicyclopentadienyllithium,[9,10,22] and chlorodimethyl(isodicyclopentadienyl)silane[13] were synthesized according to literature procedures. Elemental analyses were performed by the Service de microanalyses du L.S.E.O. (Université de Bourgogne), and ^{1}H and ^{13}C NMR

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(21) Schmid, M. A.; Alt, H. G.; Milius, W. *J. Organomet. Chem.* **1995**, *501*, 101−106.

(22) Paquette, L. A.; Charumilind, P.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1983**, *105*, 3126−3135.

Table 2. Ethylene and Propylene Polymerizations Catalyzed with 5-MAO

monomer	T_p (°C)	MAO	time (min)	yield (g)	cat (μmol)	A (g P/((mol Zr)·[P, bar]·h))	T_m	(rrrr)
ethylene	20	1:1000	5	6.2	37	500 000	135	
propylene	20	1:1000	20	1.26	30	30 000	160	90.5
propylene	70	1:1000	60	2	34	15 000		17.4

spectra were recorded with a Bruker DRX500 spectrometer (Centre de Spectroscopie Moléculaire de l'Université de Bourgogne). Isodicyclopentadienyl methano- and ethano-bridged NMR chemical assignments were not possible by simple first-order approximation and the coupling constants could no longer be obtained by a simple spacing measurement. For this reason, methano and ethano bridge protons are described as double multiplets (dm). Mass spectra were determined with a KRATOS concept IS instrument (Centre de Spectroscopie Moléculaire de l'Université de Bourgogne); EI at 70 eV.

Ethylene and propylene polymerization reactions were carried out in a 250-mL Büchi glass autoclave equipped with a magnetic stirrer. In the autoclave, MAO was added to 60 mL of dry toluene under argon. The reactor was maintained at the desired temperature and pressurized with the appropriate monomer (1 bar) for 30 min. A solution of catalyst (20−50 mg) in toluene (5 mL) was then added via a syringe. After the addition, the autoclave was pressurized with a monomer pressure of 4 bar and the reaction mixture was stirred for 1 h. During the polymerization reactions, monomer was fed continuously to maintain the desired pressure. Finally, the autoclave was vented and the reaction mixture was quenched with 10% HCl in methanol (30 mL) and stirred for 1 h. The precipitated polymer was collected by filtration, washed several times with water and methanol to remove Al residues, and dried under vacuum for 1 day to constant weight.

DSC experiments: A 10-mg sample of polymer were weighted and sealed in aluminum crucibles. The samples were scanned to 160 °C in a Mettler 182E calorimeter at a heating rate of 8 deg/min to remove previous thermal history. The samples were then cooled to 50 °C at a rate of 10 deg/min and heated again up to 160 °C at a heating rate of 8 deg/min where the thermograms were recorded.

^{13}C{^{1}H} NMR spectra were recorded with dilute (<10 mg/mL) polymer solution in 2,4,6-trichlorobenzene/C_6D_6 (4/1) at 70 °C with typical NMR program data for polymer measurements.[23,24] The pentad distribution in the methyl pentad region is found to be [mmmm], 0; [mmmr], 0; [rmmr], 0.5; [mmrr], 2.2; [xmrx], 1.7; [mrmr], 0.9; [rrrr], 90.5; [mrrr], 3; [mrrm], 1.2 at 20 °C and [mmmm], 2.8; [mmmr], 7.2; [rmmr], 6.2; [mmrr], 15.7; [xmrx], 21.0; [mrmr], 8.1; [rrrr], 17.4; [mrrr], 14.5; [mrrm], 7.1 at 70 °C.

(Isodicyclopentadienyl)(9-fluorenyl)dimethylsilane (7). A solution of fluorenyllithium (10.53 mmol, 1.81 g) in dry diethyl ether (20 mL) was slowly added to a solution of chlorodimethyl(isodicyclopentadienyl)silane **(6)** (10.53 mmol, 2.36 g) in diethyl ether (20 mL) cooled to −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. Elimination of lithium chloride by filtration and removal of the solvent gave a viscous red brown oil (8.97 mmol, 3.17 g, 69%).

^{1}H NMR (C_6D_6) δ 7.89 (d, 2H, $J_{HH} = 4$ Hz, 1-, 8-H), 7.61 (d, 2H, $J_{HH} = 4$ Hz, 4-, 5-H), 7.33−7.40 (br m, 4H, 3-, 6-, 2-, 7-H), 5.69 (br s, 2H, peripheral), 3.89 (s, 1H, 9-H), 3.54 (br s, 1H, central), 3.10 (br s, 2H, bridgehead), 1.85 (dm, 1H, $J_{HH} = 8.99$ Hz, *syn*-methano bridge), 1.70 (dm, 2H, $J_{HH} = 7.13$ Hz, *exo*-ethano bridge), 1.53 (dm, 1H, $J_{HH} = 9.2$ Hz, *anti*-methano bridge), 1.34 (dm, 2H, $J_{HH} = 7.06$ Hz *endo*-ethano bridge), −0.22 (s, 6H, SiCH_3). ^{13}C{^{1}H} NMR (C_6D_6) δ 155.3 (quaternary), 146.0 (10-, 13-C), 141.2 (11-, 12-C), 126.7 (3-, 6-C), 126.0 (2-, 7-C), 124.7 (4-, 5-C), 120.6 (1-, 8-C), 115.9 (peripheral), 50.5 (central), 46.5 (methano bridge), 44.0 (9-C), 39.6 (bridgehead), 29.2 (ethano bridge), −5.7 (s, SiCH_3). MS, m/z (relative intensity): 254 (M^+, 27), 339 (($M - Me)^+$, 2), 240 (($C_{13}H_9$-$SiMe_3)^+$, 100), 222 (($M -$ isodiCp$)^+$, 42).

Dimethylsilene(η^3-fluorenyl)(η^5-isodicyclopentadienyl)zirconium Dichloride (5). To a solution of **7** (9.68 mmol, 3.42 g) in 20 mL of diethyl ether at −78 °C was slowly added *n*-butyllithium (20 mmol, 12.5 mL of a 1.6 M solution in hexane). The mixture was allowed to warmed to room temperature and the orange yellow suspension was refluxed overnight. The yellow precipitate was filtered off, washed 3 times with diethyl ether, and dried in a vacuum (9.2 mmol, 95%). After the yellow powder was placed in 20 mL of diethyl ether at −78 °C, the suspension was treated gradually with solid zirconium tetrachloride (10.12 mmol, 2.36 g). The mixture was warmed to room temperature and stirred for 72 h. Evaporation of the solvent, washing with 15 mL of toluene, and filtration of the resulting orange suspension afforded an orange powder (62%, 5.7 mmol, 2.93 g). Dissolution of the powder with 120 mL of THF and cooling to 0 °C for 24 h and −30 °C for 2 days afforded orange crystals suitable for X-ray measurement. ^{1}H NMR (C_6D_6) δ 8.03 (dt, $J_{HH} = 8.36$, 1 Hz, 2H, 1-, 8-H), 7.59 (tm, $J_{HH} = 7.53$ Hz, 2H, 2-, 7-H), 7.45 (dt, $^2J_{HH} = 8.53$ Hz, 4-, 5-H), 7.23 (tm, $J_{HH} = 7.64$ Hz, 2H 3-, 6-H), 5.15 (s, 2H, peripheral), 3.69 (m, 4H, OCH_2), 3.23 (br s, 2H, bridgehead), 2.51 (dm, $^2J_{HH} = 9.23$ Hz, 1H, *syn*-methano bridge), 1.62 (dm, $^2J_{HH} = 6.92$ Hz, 2H, *exo*-ethano bridge), 1.52 (m, 4H, OCH_2CH_2), 1.32 (dm, $^2J_{HH} = 9.29$ Hz, 1H, *anti*-methano bridge), 1.01 (dm, $^2J_{HH} = 7.35$ Hz, 2H, *endo*-ethano bridge), 0.74 (s, 6H, SiCH_3). ^{13}C{^{1}H} NMR (C_6D_6) δ 157.7 (quaternary), 128.7 (3-, 6-C), 126.8 (2-, 7-C), 125.5 (1-, 8-C), 124.0 (4-, 5-C), 104.5 (central), 104.0 (peripheral), 65.3 (OCH_2), 50.7 (methano bridge), 41.2 (bridgehead), 28.3 (ethano bridge), 25.7 (OCH_2CH_2), −0.9 (s, SiCH_3). Fluorene quaternary carbons are not detected in the spectrum. MS, m/z (rel intensity): 514 (M^+, 1), 486 (($M -$ Si$)^+$, 2), 354 (isodiCp$SiMe_2C_{13}H_9^+$, 22), 189 (isodiCp$SiMe_2^+$, 100).

X-ray Structure Determination. All work was done at 200 K with an Oxford Cryosystems Cryostream Cooler. Data integration was done with Denzo,[25] and scaling and merging of the data was done with Scalepack..[25] The teXsan[26] package indicated the space group to be $P2_1/n$. The structure was solved by the direct methods procedure in SHELXS-86.[27] Most of the molecule was located on the electron density map, with the remainder of the atoms found by standard Fourier methods. Full-matrix least-squares refinements based on F^2 were performed in SHELXL-93.[28] Beside the Zr complex, the asymmetric unit contains a solvent molecule of THF.

The hydrogen atoms were included in the model at calculated positions by using a riding model with $U(H) = 1.2 \cdot U_{eq}$(attached atom). The methyl group hydrogen atoms were added at calculated positions by using a model with $U(H) = 1.5 \cdot U_{eq}$(bonded carbon atom), and the torsion angle that defines the orientation of each group about the Si−C bond was

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(23) Hansen, E. W.; Blom, R.; Bade, O. M. *Polymer* **1997**, *38*, 4295−4304.

(24) Busico, V.; Cipullo, R.; Monaco, G.; Vacatello, M.; Segre, A. L. *Macromolecules* **1997**, *30*, 6251−6263.

(25) Otwinovski, Z.; Minor, W. In *Macromolecular Crystallography*; Carter, C. W., Jr., Sweet, R. M., Eds., Ed.; Academic Press., 1997; Part A, Vol. 276, pp 307−326.

(26) *TeXsan*: Crystal Structure Analysis Package, version 1.7-2; Molecular Structure Corporation: The Woodlands, TX 1995.

(27) *SHELXS-86*: Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

(28) *SHELXL-93*: Sheldrick, G. M.; Universität Gottingen: Gottingen, Germany, 1993.

refined. Neutral atom scattering factors were used and include terms for anomalous dispersion.[29]

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Supporting Information Available: Ortep drawing, unit cell drawing, stereodrawing of the unit cell, data collection and refinement data details, crystal data details, bond lengths and angles, atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacements parameters, calculated hydrogen coordinates and isotropic displacement parameters, geometry around the Zr involving ring centroids for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C.