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## Syntheses of Polysiloxane-Bridged Dinuclear Metallocenes and Their Catalytic Activities

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The polysiloxane-bridged dinuclear metallocenes  $[(\text{SiMe}_2\text{O})_n\text{-SiMe}_2(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7\text{ZrCl}_2)_2]$  ( $n=1$  (**7**), 2 (**8**), 3 (**9**)) have been generated as a model complex for the immobilized metallocene at silica surface by treating the respective disodium salts of the ligands with 2 equivalents of  $(\text{C}_9\text{H}_7\text{ZrCl}_3)$  in THF. All three complexes are characterized by  $^1\text{H}$  NMR and measurement of metal content through ICP-MS. It turned out that the values of  $\Delta\delta=[\delta_r-\delta_p]$ , the chemical shift difference between the distal ( $\delta_d$ ) and proximal ( $\delta_p$ ) protons, for the produced dinuclear compounds (0.47 for **7**, 0.49 for **8**, and 0.5 for **9**) were larger than the  $\Delta\delta$  value of the known *ansa*-type complex holding the same ligand as a chelating one, that is just the opposite to the normal trend. In order to compare polymerization behavior of the dinuclear metallocene with the corresponding mononuclear metallocene,  $(\text{Cp})(\text{C}_9\text{H}_7\text{ZrCl}_2)$  was separately prepared. To investigate the catalytic properties of the dinuclear complexes and mononuclear metallocenes ethylene polymerization has been conducted in the presence of MMAO. The polymerization results display the typical activity dependence on polymerization temperature for all complexes. The most important feature is that the polymers from the dinuclear metallocenes represent enormously improved molecular weight compared with the polymer from the corresponding mononuclear metallocene. In addition, the influence of the nature of the bridging ligand upon the reactivities of the dinuclear metallocenes has also been observed.

### Introduction

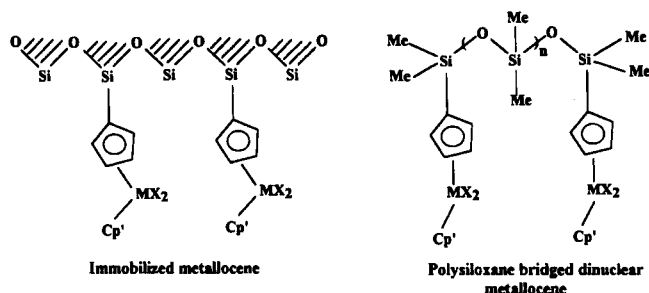
Since the discovery in 1980 that in the presence of MAO  $\text{Cp}_2\text{ZrCl}_2$  acts as a homogeneous catalyst for ethylene polymerization, many efforts have been devoted to the development of various kinds of metallocenes that not only polymerize  $\alpha$ -olefins but also polymerize polar monomers.<sup>1</sup> As a consequence there have been very valuable advances on both academic and industrial sides that allow a better understanding of the polymerization mechanism and of the correlation between metallocene structure and polymer properties.<sup>2</sup>

We have been interested in preparing metallocenes containing the polysiloxane moiety and probing their polymerization behaviors, since these compounds could be an adequate model to study the reactivities of an immobilized metallocene at the silica surface. Recently we reported the synthesis of polysiloxane-bridged *ansa*-metallocene<sup>3</sup> as well as dinuclear half-metallocenes<sup>4</sup> having two  $[\text{CpTiCl}_3]$  fragments, and their polymerization results. In particular, dinuclear metallocenes have attracted attention because the two metal centers may show cooperative electronic and chemical effects which could be potentially useful for the development of new metallocene catalysts. Furthermore, it is

plausible that the dinuclear metallocene complexes might be a better model to investigate characteristics of an immobilized metallocene than the corresponding mononuclear metallocene, because the immobilized metallocene could be regarded as a kind of multinuclear metallocene, as shown in Figure 1.

Recently, Patterson prepared a series of dinuclear zirconocene complexes  $[\text{X}(\text{C}_5\text{H}_4)_2][(\text{C}_5\text{R}_5\text{ZrCl}_2)_2]$  ( $\text{X}=\text{CH}_2$ ,  $\text{SiMe}_2$ ;  $\text{R}=\text{H}$ ,  $\text{CH}_3$ ), which contain two mechanically linked zirconocene dichloride units and examined the structural response of the  $[\text{SiMe}_2(\text{C}_5\text{H}_4)_2]^{2-}$  ligand to changes in the metal coordination environment.<sup>5</sup> More recently, Royo described the synthesis and characterization of dinuclear metallocene complexes of titanium with  $[\text{SiMe}_2(\text{C}_5\text{H}_4)_2]^{2-}$  as a bridging ligand.<sup>6</sup> Although some interesting dinuclear metallocene complexes of titanium and zirconium are well represented, relatively few publications have demonstrated the utilization of dinuclear metallocene as an olefin polymerization catalyst.<sup>7</sup>

We are especially interested in reactivity studies aiming at how the mutual participation of two metal centers modifies the reactivity patterns normally shown by the corresponding mononuclear fragments according to the nature

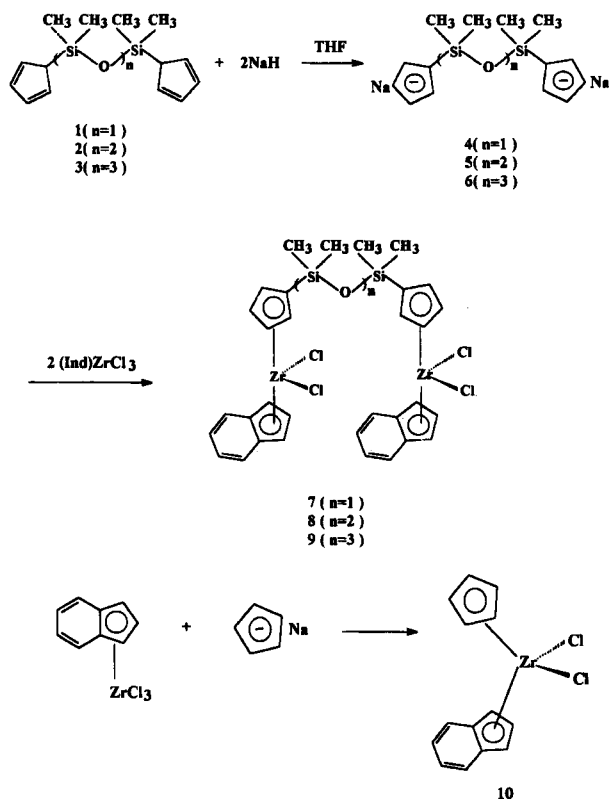


**Figure 1.** Illustrated structure of immobilized metallocene and polysiloxane bridged dinuclear metallocene as a model compound.

of the bridges in terms such as length and structure. In this context we have synthesized a series of dinuclear metallocenes containing polysiloxane units as a bridging ligand and conducted ethylene polymerization with these complexes to examine not only the effect of bridge nature on catalyst property, but also the characteristics of dinuclear metallocenes.

## Results and Discussion

**Synthesis and characterization.** The polysiloxane-bridged dinuclear metallocenes  $[(\text{SiMe}_2\text{O})_n\text{-SiMe}_2(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$  ( $n=1$  (**7**),  $2$  (**8**),  $3$  (**9**)) can be conveniently prepared in modest yield (40-50%) by treating the respective disodium salts of the ligands with 2 equivalents of  $(\text{C}_9\text{H}_7)\text{ZrCl}_2$  in THF. In order to look at the reactivity differences between a dinuclear and a mononuclear complex,



**Scheme 1.**

the corresponding mononuclear complex **10** is generated separately according to the procedure shown in Scheme 1. All compounds **7**, **8**, and **9** are separated as pale yellow powders which are soluble in THF and methylene chloride but poorly soluble in toluene and diethyl ether. They are thermally quite stable in solution and can be heated to 110 °C without noticeable decomposition. Metal content measurements are consistent with the proposed empirical formula (Experimental Section). The  $^1\text{H}$  NMR spectra of the complexes provide firm support for the assigned structure.  $^1\text{H}$  NMR spectrum of compound **7** indicates the expected resonances for the bridging tetramethyldisiloxanediybis(cyclopentadienyl) ligand which appear as two sets of pseudotriplets, at  $\delta$  6.52 and  $\delta$  6.05 with a  $J^{\text{H-H}}$  value of 2.4 Hz due to an AA'BB' system and a singlet at 0.31 ppm for Si-CH<sub>3</sub>. Similar behavior is observed for compounds **8** and **9**. The low field pseudotriplets at  $\delta$  6.56 and  $\delta$  6.07 are assigned to the cyclopentadienyl protons of the bridging ligand. The remaining assignments are summarized in Table 1.

The value of  $\Delta\delta=[\delta_d-\delta_p]$ , the chemical shift difference between the distal ( $\delta_d$ ) and proximal ( $\delta_p$ ) protons, has been used as a convenient spectroscopic parameter for distinguishing between the bridging and chelating modes of coordination for a mechanically linked bis(cyclopentadienyl) ligand.<sup>5,6</sup> Generally it is known that the magnitude of  $\Delta\delta$  ob-

**Table 1.** Summary of  $^1\text{H}$  NMR data for the synthesized polysiloxane dinuclear metallocenes and mononuclear  $(\text{Cp})(\text{Ind})\text{ZrCl}_2$

Compound	Solvent	Assignment	$^1\text{H}$ NMR
$[(\text{SiMe}_2\text{O})\text{SiMe}_2(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ ( <b>7</b> )	$\text{CDCl}_3$	$\text{C}_5\text{H}_4$	6.52 (t, 2.4 Hz, 4H)
		$\text{C}_9\text{H}_7$	6.05 (t, 2.4 Hz, 4H)
			7.63 (m, 4H)
			7.28 (m, 4H)
			6.82 (t, 3.3 Hz, 2H)
			6.47 (d, 3.3 Hz, 4H)
$[(\text{SiMe}_2\text{O})_2\text{SiMe}_2(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ ( <b>8</b> )	$\text{CDCl}_3$	$\text{C}_5\text{H}_4$	6.56 (t, 2.4 Hz, 4H)
		$\text{C}_9\text{H}_7$	6.07 (t, 2.4 Hz, 4H)
			7.63 (m, 4H)
			7.28 (m, 4H)
			6.85 (t, 3.3 Hz, 2H)
			6.49 (d, 3.3 Hz, 4H)
$[(\text{SiMe}_2\text{O})_3\text{SiMe}_2(\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ ( <b>9</b> )	$\text{CDCl}_3$	$\text{C}_5\text{H}_4$	6.57 (t, 2.4 Hz, 4H)
		$\text{C}_9\text{H}_7$	6.07 (t, 2.4 Hz, 4H)
			7.63 (m, 4H)
			7.28 (m, 4H)
			6.85 (t, 3.3 Hz, 2H)
			6.49 (d, 3.3 Hz, 4H)
$(\text{C}_5\text{H}_5)(\text{C}_9\text{H}_7)\text{ZrCl}_2$ ( <b>10</b> )	$\text{CDCl}_3$	$\text{C}_5\text{H}_5$	0.34 (s, 12H)
			0.02 (s, 6H)
		$\text{C}_5\text{H}_5$	6.57 (t, 2.4 Hz, 4H)
		$\text{C}_9\text{H}_7$	6.07 (t, 2.4 Hz, 4H)
			6.57 (t, 2.4 Hz, 4H)
$(\text{C}_5\text{H}_5)(\text{C}_9\text{H}_7)\text{ZrCl}_2$ ( <b>10</b> )	$\text{CDCl}_3$	$\text{C}_5\text{H}_5$	6.16 (s, 5H)
		$\text{C}_9\text{H}_7$	7.68 (m, 2H)
			7.30 (m, 2H)
			6.91 (t, 3.3 Hz, 1H)
			6.53 (d, 3.3 Hz, 2H)

**Table 2.**  $\Delta\delta$  value for titanium and zirconium dinuclear metallocenes

Complex	Solvent	$\delta$ for $C_5H_4$	$\Delta\delta$	ref.
7, $[O(SiMe_2C_5H_4)_2][(C_9H_7)ZrCl_2]_2$	$CDCl_3$	6.52, 6.05	0.47	this work
8, $[SiMe_2(OSiMe_2C_5H_4)_2][(C_9H_7)ZrCl_2]_2$	$CDCl_3$	6.56, 6.07	0.49	this work
9, $[O\{O(SiMe_2)C_5H_4\}_2][(C_9H_7)ZrCl_2]_2$	$CDCl_3$	6.57, 6.07	0.50	this work
11, $[SiMe_2(C_5H_4)_2][TiCl_3]_2$	$CDCl_3$	7.23, 7.09	0.14	6
12, $[SiMe_2(C_5H_4)_2][(C_5H_5)TiCl_2]_2$	$CDCl_3$	6.87, 6.62	0.25	6
13, $[SiMe_2(C_5H_4)_2][(C_5Me_5)TiCl_2]_2$	$CDCl_3$	6.42, 6.08	0.34	6
14, $[O(SiMe_2C_5H_4)_2][TiCl_3]_2$	$CDCl_3$	7.22, 7.06	0.16	4
15, $[SiMe_2(OSiMe_2C_5H_4)_2][TiCl_3]_2$	$CDCl_3$	7.23, 7.05	0.18	4
16, $[SiMe_2(C_5H_4)_2][(C_5H_5)ZrCl_2]_2$	$CDCl_3$	6.60, 6.44	0.16	5
17, $[SiMe_2(C_5H_4)_2][(C_5Me_5)ZrCl_2]_2$	$C_6D_6$	6.22, 5.90	0.32	5
18, $[CH_2(C_5H_4)_2][(C_5H_5)ZrCl_2]_2$	$CD_2Cl_2$	6.37, 6.23	0.14	5
19, $[CH_2(C_5H_4)_2][(C_5Me_5)ZrCl_2]_2$	$C_6D_6$	5.98, 5.65	0.33	5
20, $[SiMe_2(OSiMe_2C_5H_4)_2][(C_5H_5)ZrCl_2]_2$	$CDCl_3$	6.74, 6.52	0.22	3
21, $O(SiMe_2C_5H_4)_2ZrCl_2$	$CDCl_3$	6.84, 6.54	0.30	3
22, $SiMe_2(OSiMe_2C_5H_4)_2ZrCl_2$	$CDCl_3$	6.68, 6.59	0.09	3

served for the dinuclear metallocene retaining the bridging mode of coordination is smaller than that for the mononuclear metallocene retaining the chelating mode of coordination. On this basis the values of  $\Delta\delta$  for the prepared compounds have been measured and displayed in Table 2, along with the other values reported. The indicated  $\Delta\delta$  values are 0.47 for **7**, 0.49 for **8**, and 0.50 for **9**. As shown in Table 2, these are found to be greater than other numbers observed for dinuclear complexes. In addition, the  $\Delta\delta$  value of 0.47 for **7** holding tetramethylsiloxanediylbis(cyclopentadienyl) as a bridging ligand is actually greater than the  $\Delta\delta$  value of 0.3 for **21** holding the same ligand as a chelating one. That is just the opposite to the normal trend. This reversal is further evidenced by a comparison of  $\Delta\delta$  for the dinuclear metallocene **8** (0.49) and its corresponding mononuclear metallocene **22** (0.09). Actually this reversal behavior had already been described for compounds containing the double-dimethylsilyl-bridged metallocene complexes.<sup>8</sup> These results indicate that the  $\Delta\delta$  value cannot be generally used to predict modes of coordination, particularly in case of complexes possessing a relatively longer bridging ligand than the well-known dimethylsilyl, or methylene bridge. At the moment the detailed correlation between the value of  $\Delta\delta$  and the coordination mode can not seem to be explained readily, but several points can be noted. In the dinuclear metallocenes,  $\Delta\delta$  increases steadily as the bridging ligand becomes longer, while the reverse is observed for mononuclear ones. This spectral feature can be shown clearly from the  $\Delta\delta$  values of 0.14, 0.16, and 0.18 for complexes **11**, **14**, and **15**, respectively, holding two  $[CpTiCl_3]$  units. The same trend was also demonstrated in the case of complexes **18**, **16**, and **20** containing two  $[Cp_2ZrCl_2]$  units.

A second feature associated with the value of  $\Delta\delta$  is that the type of free cyclopentadienyl ligand (*i.e.*,  $C_5H_5$  vs  $C_5Me_5$  vs  $C_9H_7$ ) appears to be the predominant influence on the value of  $\Delta\delta$ . For instance, replacement of  $C_5H_5$  with  $C_5Me_5$  doubled the magnitude of  $\Delta\delta$  from 0.16 for **16** to 0.32 for **17**. This behavior is aggravated by the substitution of  $C_9H_7$  for  $C_5H_5$ , resulting in a change from 0.22 for **20** to 0.49 for **8**. It is believed that the presence of an indenyl group as a free cyclopentadienyl derivative ligand is responsible for the

unusually large  $\Delta\delta$  value of the dinuclear metallocene studied in this work. Another relevant explanation of the large  $\Delta\delta$  value for the polysiloxane-bridged dinuclear metallocene complexes is the relatively small steric interaction around the metallic center due to the increased separation between the linked cyclopentadienyl rings, as Royo suggested.<sup>6</sup>

**Polymerization.** To investigate the catalytic properties of dinuclear complexes, ethylene polymerization has been conducted in the presence of MMAO. In a series of experiments, the catalysts were used in toluene at 30, 40, and 55 °C and a constant Al/Zr ratio. A comparison of the polymerization data in Table 3 shows the typical activity dependence on polymerization temperature ( $T_p$ ) for all complexes. All the complexes exhibit maximum activity at 40 °C. However, above and below 40 °C the values of ethylene polymerization activities decrease sharply. Complex **8** with trisiloxane linkage exhibits the greatest activity among dinuclear metallocenes. It is worth noting that the longer the bridge of the dinuclear complex in the polymerization system the greater the activity became. The most important feature is that polymers produced by dinuclear metallocene complexes represent improved molecular weight compared with polymers by corresponding mononuclear metallocene. The dinuclear complexes generate polyethylene with at least 2-3 times greater molecular weight than the corresponding mononuclear complex. The metallocene holding the shortest bridging ligand generates polyethylene with the highest molecular weight. Practically, this is just opposite to Mullhaupt's observation.<sup>7</sup> He found that the molecular weight of polypropylene obtained with phenylene bridged

**Table 3.** Results of ethylene polymerization with the dinuclear and mononuclear complexes

Catalyst	Activity	$M_w (\times 10^{-3})$	$M_w/M_n$	$T_m$ (°C)
Complex <b>7</b>	1762	450	4.3	136
Complex <b>8</b>	2187	442	4.6	134
Complex <b>9</b>	2451	350	3.4	135
Complex <b>10</b>	2647	163	2.7	135

Polymerization temperature=40 °C,  $[Al]/[Zr]=10,000$ , Activity=Kg-PE/mol-Zr-h-atm

dinuclear metallocene is markedly lower than that of polypropylene with the corresponding mononuclear compound. He explained this outcome based on the electronically coupled interaction between two cationic active centers through the phenylene bridge. However, in the case of the dinuclear complexes in this work, it is unlikely that the same kind of interaction as Mullhaupt's can be operative because the polysiloxane bridge does not seem to be effective in transferring information about electron deficiency from one center to the other. Actually similar tendency has been observed by M.L.H. Green with a variety of dimethylsilyl-,  $-\text{Si}(\text{Me})_2-$ , bridged dinuclear metallocenes.<sup>10</sup> We propose steric congestion between two metallic centers as responsible for the generation of higher molecular weight polyethylene by the polysiloxane-bridged dinuclear metallocene. The closer distance between the two active sites of the relatively shorter bridged dinuclear metallocene should make more steric disturbance than the longer bridged dinuclear metallocene. It is understandable that a more sterically hindered metallic center produces higher molecular weight polymer as a consequence of more difficult  $\beta$ -H elimination. Another interesting point is that the dinuclear metallocenes give rise to a somewhat broadened molecular weight distribution. The value of  $M_w/M_n$  in Table 3 ranges from 3.4 to 4.6, which are pretty big numbers for the polyethylene formed by the metallocene catalyst.

From the above results some important points to characterize the dinuclear metallocene can be noted. The first point is that the dinuclear metallocene shows different properties from the known, corresponding mononuclear metallocene, which indicates that the dinuclear complex can be usefully employed to make polymers displaying enhanced or modified properties distinguished from the known polymers. For instance, a polymer with high molecular weight and wide molecular weight distribution can be synthesized by use of a dinuclear metallocene. This should be one of the most important advantages of the dinuclear metallocenes to think about the importance of the molecular weight and molecular weight distribution to dominate polymer property. The other point is that the nature of the bridging ligand really exerts an influence upon the reactivities of the dinuclear metallocenes. The different behavior observed in this work and Mullhaupt's work clearly demonstrates this feature. In summary, the development of new dinuclear metallocenes as an olefin polymerization catalyst can be very valuable to explore new polyolefins exhibiting distinct and improved properties from the existing mononuclear metallocene polymers.

## Experimental Section

All reactions were carried out under a dry, oxygen-free atmosphere using standard Schlenk techniques with a double manifold vacuum line. Nitrogen gas was purified by passage through a column of molecular sieve (4 Å) and Drierite (8 mesh). Tetrahydrofuran, diethylether, toluene, hexane, and pentane were distilled from sodium/benzophenone ketyl prior to use. Methylene chloride was distilled from phosphorous pentoxide prior to use. White filtering aid (celite) was stored in a 130 °C oven. 1,3-Dichlorotetra-methyl-disiloxane, 1,5-dichlorohexamethyltrisiloxane and 1,7-

dichlorooctamethyltetrasiloxane purchased from United Chemical Technologies were used after distilling from calcium hydride. CpLi, CpNa (2.5 Mol solution in THF), and TIOEt were used as purchased from Aldrich. Modified methylaluminoxane (MMAO, Type-4, 6.4 wt% Al, Akzo, U. S.A) was used without further purification. NMR spectra were recorded at 300 MHz on a Bruker ARX-300 FT-NMR spectrometer. Metal content was measured by Jobin-Yvon 38 Plus ICP Emission Spectrometer. IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer between 4000 and 200  $\text{cm}^{-1}$ . Melting point of polymers were measured by means of differential scanning calorimetry (DSC) (Dupont TA 2000) at 20 °C/min. Molecular weight and molecular weight distribution of polymers were determined by gel permeation chromatography (GPC) (Waters 150C) in 1,2,4-trichlorobenzene at 135 °C and data were analyzed using polystyrene calibration curves. All the dimetallic salts<sup>4-6</sup> and (Indenyl)ZrCl<sub>3</sub><sup>9</sup> were synthesized according to literature methods.

### Synthesis of $[\text{O}(\text{SiMe}_2\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ , 7.

To a solution of (Indenyl)ZrCl<sub>3</sub> (2.45 g, 7.8 mmol) in 150 mL THF at RT was slowly added  $[\text{O}(\text{SiMe}_2\text{C}_5\text{H}_4)_2]\text{Na}_2$  (1.2 g, 3.9 mmol) in 100 mL THF. The color of the solution gradually turns pale green from dark orange. After addition, the solution was warmed to RT and stirred for 1 hr followed by heating overnight at 60 °C. After removal of NaCl by filtration solvent was evaporated under vacuum. The resulting yellowish solid was extracted with hot toluene through the Soxhlet extractor. The residual solid inside the thimble filter was dried and recrystallized in chloroform to give the product as a pale yellow solid in 45% yield. mp 257 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.63 (m, 4H), 7.28 (m, 4H), 6.83 (t, 3.3 Hz, 2H), 6.52 (t, 2.4 Hz, C<sub>5</sub>H<sub>4</sub>), 6.47 (d, 3.3 Hz, 2H), 6.05 (t, 2.4 Hz, C<sub>5</sub>H<sub>4</sub>), 0.31 (s, 12H), Zr content; Calcd.: 22.40, Found: 20.56, IR (KBr)  $\text{cm}^{-1}$  3102, 2960, 1412, 1257, 1089, 1040, 824, 799, 754.

### Synthesis of $[\text{SiMe}_2(\text{OSiMe}_2\text{C}_5\text{H}_4)_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ , 8.

This reaction proceeded in an analogous fashion to the above reaction with the following exceptions:  $[(\text{OSiMe}_2\text{C}_5\text{H}_4)_2]\text{Na}$  (1.1 g, 2.9 mmol) was used in place of  $[\text{O}(\text{SiMe}_2\text{C}_5\text{H}_4)_2]\text{Na}_2$  (1.2 g, 3.9 mmol) and 5.8 mmol (1.8 g) of (Indenyl)ZrCl<sub>3</sub> was used instead of 7.8 mmol. Extraction from toluene gave pale yellow solid of 8 (43% yield). mp 216 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.63 (m, 4H), 7.28 (m, 4H), 6.85 (t, 3.3 Hz, 2H), 6.56 (t, 2.4 Hz, C<sub>5</sub>H<sub>4</sub>), 6.49 (d, 3.3 Hz, 4H), 6.07 (t, 2.4 Hz, C<sub>5</sub>H<sub>4</sub>), 0.34 (s, 12H), 0.02 (s, 6H), Zr content; Calcd.: 20.53, Found: 20.45, IR (KBr,  $\text{cm}^{-1}$ ) 3102, 2960, 1412, 1257, 1089, 1040, 824, 799, 754.

### Synthesis of $[\text{O}\{\text{O}(\text{SiMe}_2)_2\text{C}_5\text{H}_4\}_2][(\text{C}_9\text{H}_7)\text{ZrCl}_2]_2$ , 9.

The method similar to those used to make 7 were also applied. The only exception was introduction of  $[\text{O}\{\text{O}(\text{SiMe}_2)_2\text{C}_5\text{H}_4\}_2]\text{Na}_2$  in place of  $[\text{O}(\text{SiMe}_2\text{C}_5\text{H}_4)_2]\text{Na}_2$ . The final product 10 was separated in 43% yield as a pale green solid. mp 217 °C, 43% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.63 (m, 4H), 7.28 (m, 4H), 6.85 (t, 3.3 Hz, 2H), 6.57 (t, 2.4 Hz, C<sub>5</sub>H<sub>4</sub>), 6.49 (d, 3.3 Hz, 4H), 6.07 (t, 2.4 Hz, C<sub>5</sub>H<sub>4</sub>), 0.34 (s, 12H), 0.02 (s, 12H), Zr content; Calcd.: 18.96, Found: 19.56, IR (KBr,  $\text{cm}^{-1}$ ) 3102, 2960, 1412, 1257, 1089, 1040, 824, 799, 754.

**Preparation of (Indenyl)(Cp)ZrCl<sub>2</sub>, 10.** A solution of (Indenyl)ZrCl<sub>3</sub> (0.94 g, 3 mmol) in 150 mL THF was

treated with a stoichiometric amount of CpNa (1.5 mL of 2.5 mol solution in THF) slowly at RT. The color of solution turns red orange with a precipitation of NaCl. After being stirred for 3 h, the salt was removed by filtration followed by solvent evaporation under vacuum. The resulting yellowish solid was extracted with ether using the Soxhlet extractor. The residual solid inside the thimble filter was dried to give the product as a pale green solid in 35% yield. mp 168 °C,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.68 (m, 2H), 7.30 (m, 2H), 6.91 (t, 3.3 Hz, 1H), 6.53 (d, 3.3 Hz, 2H), 6.16 (s,  $\text{C}_5\text{H}_5$ ), Zr content; Calcd.: 26.64, Found: 24.84, IR ( $\text{KBr}$ ,  $\text{cm}^{-1}$ ) 3102, 1439, 1342, 1014, 821, 750, 449.

**Polymerization.** All operations were carried out under the nitrogen atmosphere. In a 400 mL glass reactor were introduced sequentially the proper amount of toluene and MMAO solution and then the system was saturated with ethylene. With continuous flow of ethylene, the polymerization was initiated by injecting the solution of metallocenes. After 2h polymerization polyethylene was precipitated in acidified methanol.

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