

# Synthesis of Double Silylene-Bridged Binuclear Metallocenes and Their Cooperation Effect During Ethylene Polymerization and Ethylene/1-Hexene Copolymerization

Puke Mi,<sup>1</sup> Sheng Xu,<sup>1</sup> Liangduan Qu,<sup>1</sup> Zhang Deshun,<sup>2</sup> Chen Qian,<sup>2</sup> Wang Sihan<sup>2</sup>

<sup>1</sup>Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

<sup>2</sup>Daqing Chemical Engineering Research Center, Institute of Petrochemical Engineering, PetroChina Company Limited, Daqing Heilongjiang 163714, People's Republic of China

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**ABSTRACT:** Novel double silylene-bridged binuclear Group 4 metallocene complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{MCl}_2]_2[\mu, \mu\text{-}(\text{SiMe}_2)_2(\eta^5\text{-RC}_5\text{H}_2)_2]$  [R = Me, M = Zr (1); R = allyl, M = Ti (2); R = allyl, M = Zr (3); R = <sup>n</sup>Bu, M = Ti (5); R = Me<sub>3</sub>Si, M = Zr (6)] and  $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{ZrCl}_2]_2[\mu, \mu\text{-}(\text{SiMe}_2)_2(\eta^5\text{-allyl-C}_5\text{H}_2)_2]$  (4) were synthesized by the reaction of CpMCl<sub>3</sub> (M = Ti, Zr) with  $[\mu, \mu\text{-}(\text{SiMe}_2)_2(\eta^5\text{-RC}_5\text{H}_2)_2]^{2-}(\text{L}^{2-})$  in THF, and they were all well characterized by <sup>1</sup>H-NMR, MS, and EA. When activated with methylaluminoxane (MAO), this series complexes are active catalysts for Ethylene polymerization (Complex 3,  $3.86 \times 10^6$  g-PE/

mol-M h, Al/Zr = 500) and copolymerization of ethylene with 1-hexene (Complex 3,  $30.87 \times 10^5$  g-polymer/mol-M h, 1-hexene content in polymer 2.34 mol %, Al/Zr = 1000). The result of polymerization implies that there is a cooperative effect between the two metals in the double-bridged binuclear molecules. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 21–26, 2011

**Key words:** 65306 metallocene; polymerization; cooperative effect

## INTRODUCTION

In the past decades binuclear metallocene catalysts have been developed, in which the structure and rigidity of the bridge between the two cyclopentadienyl rings(Cp) greatly influence the catalytic behavior of these catalysts.<sup>1</sup> Actually, many mono-bridged Group 4 metallocenes complexes<sup>2</sup> have been prepared, but few of them have true synergistic reactivity, because the relative orientation between the two metal centers changes in an uncontrolled manner due to rotation around the B-Cp bond (B = bridge atom). This rotation does not allow any cooperative effect. In 2002, Marks<sup>3</sup> reported the enhancement of enchainment cooperative effect between different single-site olefin polymerization catalysts by ion pairing with a binuclear cocatalyst. That is when two reactive metal centers are held close by a double anion cocatalyst the close proximity offers the opportunity to produce cooperative chemical behavior.

A broadened molecular weight distribution (MWD) polyolefin was obtained with high comonomer incorporation.<sup>4</sup> In 2005, Marks<sup>5</sup> found that bulky hindered isoalkene comonomer can be incorporated in large percentages into polyethylene backbones via coordination polymerization processes carried out by two metal center synergistic effects and such proximity effects are highly cocatalyst and solvent sensitive.<sup>6</sup> However, the catalyst nuclearity effects was also found in bimetallic Group 4 phenoxyiminato catalysts.<sup>7,8</sup> In 2007, the Marks and Amin<sup>9</sup> studied the scope and mechanism of simultaneous polyolefin branching and functional group introduction via binuclear organotitanium-mediated ethylene polymerization. Actually, all the binuclear catalysts Marks investigated were mono-bridged constrained geometry complexes (CGC) or rigid bimetallic phenoxyiminato complexes. On the other hand, double-bridged bisCp ligands restrict the relative orientation of the two metals in the corresponding bimetallic complexes,<sup>10,11</sup> and offer a rigid system in which the metal can bind to the same or opposite faces of the bisCp ligands moiety. Among these types of complexes, the double Me<sub>2</sub>Si bridged bisCp metal complexes, including mononuclear and binuclear types have been studied and summarized in Huang's article.<sup>12</sup> They<sup>12–15</sup> found that single-bridged/

Correspondence to: S. Xu (xusheng@ecust.edu.cn).

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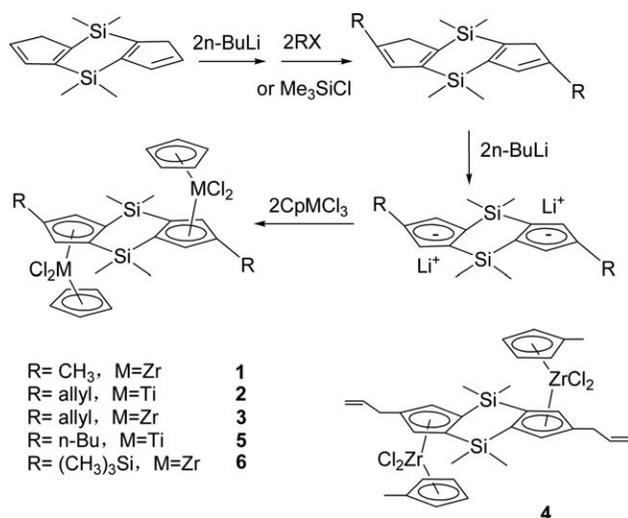
double-bridged hetero-binuclear or homo-binuclear titanium complexes with differently substituted Cp rings gave good results on the olefin polymerizations. In 2007, Xu et al.<sup>12</sup> synthesized binuclear zirconium complexes with  $[\mu, \mu-(\text{Me}_2\text{Si})_2(\eta^5\text{-C}_5\text{H}_3)_2]^{2-}$  as a bridging unit to increase the stereo rigidity of the complexes  $(\eta^5\text{-RC}_5\text{H}_4\text{ZrCl}_2)_2[\mu, \mu-(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2]$ , and introduce a series of different substituents on Cp ring. They then studied their catalytic behavior for ethylene polymerization and ethylene/1-hexene copolymerization in the presence of MAO. The polymerization results indicate that these binuclear metallocenes are excellent catalysts for olefin polymerization at very low Al/Zr ratios and broad MWD polymer was obtained. For further study of catalytic activity and cooperative effects in binuclear double-bridged metallocenes, we designed and synthesized a series of double  $\text{Me}_2\text{Si}$ -bridged binuclear metallocenes with different substituents on the bridged-Cp backbone and studied their catalytic properties for olefin polymerization. Substituent effects on the two metal centers were also investigated via ethylene polymerization and copolymerization with 1-hexene.

## RESULTS AND DISCUSSION

### Synthesis and characterization of complexes 1-6

The general method to prepare complexes **1** to **6** was the reaction of 2 equiv. of  $(\eta^5\text{-RC}_5\text{H}_4)\text{MCl}_3$  [M = Ti, Zr; R = H, Me] with  $\text{Li}_2[\mu, \mu-(\text{Me}_2\text{Si})_2(\eta^5\text{-RC}_5\text{H}_2)_2]$  in THF (illustrated in Scheme 1).

All the complexes are soluble in aromatic hydrocarbons (benzene, toluene),  $\text{CH}_2\text{Cl}_2$  and THF, scarcely soluble in diethyl ether, and insoluble in alkanes. They are sensitive to air and moisture. Complexes **1-6** were characterized well by  $^1\text{H}$  NMR, MS, and EA.



**Scheme 1** The synthetic route for complexes **1-6**.

**TABLE I**  
The Effect of Ratio of Al/Zr on Ethylene Polymerization by Complexes **1-6**

Cat.	Ratio of Al/M	Act. ( $\times 10^6$ g-PE/mol-M·h)	$M_n$ ( $\times 10^5$ g/mol)
1	500	3.86	1.03
1	1,000	4.35	3.11
1	3,000	5.47	3.52
1	5,000	7.91	2.41
1 <sup>a</sup>	10,000	10.30	1.98
2	3,000	2.99	37.6
3 <sup>a</sup>	3,000	4.16	6.24
4	3,000	4.64	5.31
5	3,000	2.77	3.86
6	3,000	3.70	5.31
$\text{Cp}_2\text{TiCl}_2$	3,000	0.97	1.17
$\text{Cp}_2\text{ZrCl}_2$	3,000	4.15	0.97

Conditions: [M] = 4.0  $\mu\text{mol}$ ;  $P_{\text{ethylene}} = 1.0$  atm.,  $t = 10$  min,  $T = 50^\circ\text{C}$ ,  $V = 150$  mL, Sol. = Toluene.

<sup>a</sup> [M] = 8.0  $\mu\text{mol}$ ,  $V = 300$  mL.

All the complexes have *trans* configuration. The *cis* or *trans* configuration can be easily distinguished by the  $^1\text{H}$  NMR signals of the bridging  $\text{SiMe}_2$  units.<sup>2</sup> For the *trans* isomer all four methyl groups are equivalent and now only one signal for  $\text{Si-Me}_2$  has been observed for complexes **1-6** respectively. The parent molecular ion peaks of complexes **1-6** could not be detected in all of the Mass spectra (EI, 70 eV). The most important character in the Mass spectra is that the ion peak corresponding to the mononuclear fragment was observed in all cases, in the same manner as Huang<sup>12</sup> found for the double-bridged binuclear zirconium complexes.

For comparison purposes the earlier parent mononuclear complexes **7,9** and mono-silylene-bridged binuclear complexes **8'10** were synthesized according to literature methods (see Chart 1).<sup>16,17</sup>

### Homogeneous polymerization ethylene

When activated with MAO, all the complexes are effective catalysts for ethylene polymerization and the results are given in Table I.

From the results it is obvious that there is a direct relationship between the activity and Al/M ratio, and the activity increases as the Al/Zr ratio is augmented. It is found that catalytic activities of binuclear zirconium complexes are higher than that of  $\text{Cp}_2\text{ZrCl}_2$  under the identical conditions (a similar situation was also found for titanium complexes), and the activities of complex **1** exceed  $3.86 \times 10^6$  g-PE/mol-M h when the ratio of Al/Zr = 500. Additionally, these complexes/MAO systems keep high activity even at low ratio of Al/Zr just as Huang<sup>12</sup> found. It is noteworthy that despite the differences in substituents on the bridge Cp, alkyl, allyl, or

**TABLE II**  
The Effect of Polymerization Time on Catalytic Activity

Complex	Act Time (min)			
	10	30	60	90
1 (Me,Zr)	5.47	2.42	1.29	1.18
3 <sup>a</sup> (Allyl,Zr)	4.16	3.94	3.39	2.51
2 (Allyl,Ti)	2.99	2.37	1.47	1.09
5 (n-Bu,Ti)	2.77	0.93	0.47	0.38

Condition: [M] = 4.0  $\mu$ mol, Al/M = 3000,  $P_{\text{ethylene}}$  = 1.0 atm.,  $T$  = 50°C,  $V$  = 150 mL, *Sol.* = Toluene, Act. =  $\times 10^6$  g-PE/mol-M·h.

<sup>a</sup> [M] = 8.0  $\mu$ mol,  $V$  = 300 mL.

silane, all of the corresponding binuclear complexes display high activities for ethylene polymerization. When the ratio of Al/Zr = 3000, **3**/MAO shows the highest activity among these complexes, which implies that the substituent group on the bridged-Cp ring affected the catalytic activity remarkably. The results also imply that the steric bulkiness of the substituent causes the activities to slowly decline as the group's bulkiness increases: **1**(Me, Zr) > **4**(Allyl, Me, Zr) > **6** (Me<sub>3</sub>Si, Zr) and **2** (Allyl, Ti) > **5**(<sup>n</sup>Bu, Ti). On the other hand, when the substituent group is a potentially weakly coordinating group (Complex **2**, **3**, **4**), the catalytic activity is higher than that of the corresponding alkyl(R = alkyl). We discovered this in our former work<sup>12</sup> and attributed it to the coordination between the allyl and activated center metal and the resulting improvement in the stability of the catalyst. This postulate is supported by the polymerization results showing the effect of polymerization time on catalyst activity (see Table II). So among these catalytic systems, **3**/MAO shows the highest catalytic activity as a result of these two factors. Further research work is continuing on the mechanism.

The nonbridged mononuclear complexes **7**, **9** and mono-silylene-bridged binuclear complexes **8** and **10** were synthesized and used to compare with double

silylene-bridged binuclear complexes. The polymerization results are shown in Table III.

From Table III, it is found that molecular weights of the PE samples generated by double bridged binuclear complex **1** are different from those obtained by the mononuclear complex **9** and single Me<sub>2</sub>Si bridged binuclear complex **10**. The polymer molecular weights produced by double bridged complex **1** are higher, which means a high ratio of polymer chain propagation to termination. We ascribe the result to the different electronic environment of the metal sites due to the double bridged-Cp ligands. Hulmut<sup>18,19</sup> has once found similar phenomena and gave explanation: the small increases in the steric environment of the active centers of metallocenes often lead to increases in activity and molecular weight together, that is, the sterically congested and highly substituted metallocene displays the highest activity in the polymerization of ethylene. This leads to the conclusion that electronic effects are particularly important for the insertion reaction because of the bigger spacer lead less sterical stress in the molecule or in the catalyst ion pair with MAO. On the other hand, in 2009, Marks<sup>20</sup> analyzed the structure and reaction mechanism of proximity and cooperative effects in binuclear d<sup>0</sup> olefin polymerization catalysis offered by binuclear CGC catalysts. The results indicated that a chain growing at one metal site modifies the environment of the second metal site of the binuclear catalyst, so as to increase propagation/termination rate ratios, which in turn favor increased product molecular weight ( $M_n$ ). However, our result is not similar to Marks, but similar to Hulmut.

It is noteworthy that the polydispersities of the polymer increase from 1.55 for Cp<sub>2</sub>ZrCl<sub>2</sub> to 5.34 for complex **1** which implies there is more than one type of activated center in the binuclear polymerization system. We suggest that the two Zr atom in complex **1** are closely held by the rigid double bridged Cp rings. When the Zr(1) atom is activated

**TABLE III**  
The Result of Ethylene Polymerization by Mononuclear and Binuclear Complexes

Cat.	Act. ( $\times 10^6$ g-PE/ mol-M·h)	$M_n$ ( $\times 10^5$ g/mol)	$M_n$ ( $\times 10^4$ g/mol)	$M_w$ ( $\times 10^5$ g/mol)	$M_w/M_n$
Cp <sub>2</sub> ZrCl <sub>2</sub>	4.15	0.97	6.93	1.07	1.55
<b>9</b>	4.86	0.91	6.49	1.08	1.67
<b>10</b>	5.31	1.32	6.77	1.44	2.12
<b>1</b>	5.47	3.52	7.87	4.20	5.34
Cp <sub>2</sub> TiCl <sub>2</sub>	0.97	1.17			
<b>7</b>	1.05	1.24			
<b>8</b>	1.31	1.85	8.89	1.88	2.01
<b>2</b>	2.99	37.6	14.75	38.65	2.62

Condition: [M] = 4.0  $\mu$ mol, Al/M = 3000,  $P_{\text{ethylene}}$  = 1.0 atm.,  $T$  = 50°C,  $V$  = 150 mL, *Sol.* = Toluene.  $M_w$ ,  $M_n$ , and  $M_w/M_n$  from GPC versus polystyrene standards. GPC was carried out at 135°C and *o*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> used as solvent.

**TABLE IV**  
**The Result of Copolymerization of Ethylene with 1-Hexene**  
**Over Complexes 1–6 and 8, 10**

Cat.	Activity ( $\times 10^5$ g /mol M h)	$M_n$ ( $\times 10^4$ g /mol)	$M_n$ g/mol	$M_w$ g/mol	MWD	1-Hexene content (mol %)
1	22.85	2.44	7,285	80,285	11.02	3.11
10	15.70	1.86				0.31
2	9.89	4.57				2.31
8	1.02	2.27				0.64
3	30.87	1.42	4,901	78,085	15.93	2.34
4	5.30	1.25				2.84
5	22.92	1.96				1.98
6	23.71	1.87				2.93
Cp <sub>2</sub> ZrCl <sub>2</sub>	23.25	/				No found

Polymerization Condition:  $[M] = 4.0 \mu\text{mol}$ ;  $P_{\text{ethylene}} = 1.0 \text{ atm}$ ,  $T = 75^\circ\text{C}$ ,  $V = 150 \text{ mL}$ ,  $t = 30 \text{ min}$ , 1-hexene = 2 mL, Al/Zr = 1,000, 1-Hexene Mole percentage calculated from  $^{13}\text{C}$  NMR spectra<sup>21</sup>;  $M_w$  and MWD calculated from GPC.

by MAO and turned into the CpZr<sup>+</sup>R state, the electronic environment of the Me<sub>2</sub>Si-bridged Cp ring which linked with Zr(2) center changed accordingly, which induced the change of the polymer chain propagation/termination rate ratios on the Zr(2) center and broadened the polymer MWD.

### Copolymerization of ethylene with 1-hexene

Complexes 1–6 and 8–10 were used to copolymerize ethylene with 1-hexene in the presence of excess MAO. The results are summarized in Table IV.

Except for Complex 4, it is obvious that all the double bridged complexes are effective catalysts for ethylene/1-hexene copolymerization. Among these complexes, 3 exhibits the highest catalytic activity ( $30.87 \times 10^5$  g Polymer/mol-Zr.h) and complex 1 shows highest 1-hexene incorporation. As for complex 4 we ascribe the lower activity to steric bulkiness of substituents on both Cp ring at each metal.

The effect of bridge on activity and 1-hexene content in the polymer were tested and the results are shown in Table IV. From the results we found that double-bridged binuclear complexes 1 and 2 displayed more effective at incorporation of 1-hexene into the backbone of PE chain than that of their earlier parent monobridged complexes 10 and 8. The 1-hexene content in complex 1 is 10 times to that of complex 10, while complex 2 is four times the activity of complex 8. These results indicate that the double-bridged Cp rings, with the four methyls of the two linking Si bridged-atoms standing almost vertically to the plane consisting of the bridged-Cp rings and two Si atoms not only stabilized the two activated metal centers via a cooperative effect, but also promoted the capacity for copolymerization, which means the reduced rotation of the Cp ring of the bridging group leads to better comonomer incorpo-

ration but the large change suggests a change in the tilt of the two rings at each metal or a cooperative effect, such as Marks has described.<sup>20</sup>

## EXPERIMENTAL

### General considerations

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF), toluene, and *n*-hexane were freshly distilled from sodium-benzophenone ketyl. Halogenated solvents were distilled from P<sub>2</sub>O<sub>5</sub> under argon. Ethylene for polymerization was used after passing it through 4 Å molecular sieves. 1-Hexene was distilled over sodium under argon and stored in the presence of activated 4 Å molecular sieves. MAO was purchased from AZO Co. The zirconium complexes ( $\eta^5\text{-RC}_5\text{H}_4\text{)ZrCl}_3\cdot\text{DME}$  were synthesized from the reaction of ( $\text{RC}_5\text{H}_4\text{)SiMe}_3$  with ZrCl<sub>4</sub> according to the literature.<sup>22</sup> [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>] and Li<sub>2</sub>[ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5\text{-C}_5\text{H}_3$ )<sub>2</sub>] were synthesized by the procedure described by Huhmann.<sup>10</sup>  $^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR were recorded on a Bruker ADVANCE DMX 500 spectrometer in CDCl<sub>3</sub> (for complexes) and *o*-C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> (for polymer samples) respectively. Mass spectra were obtained using the direct insertion probe method on Micromass GCT instrument operating at 70 eV. Elemental analyses were performed on an EA-1106. GPC was obtained on PL-GPC210 at 135°C.

Synthesis of [ $(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2$ ]<sub>2</sub>[ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5\text{-MeC}_5\text{H}_2$ )<sub>2</sub>] (1)

To a solution of [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>] (1572 mg, 6.44 mmol) in 50 mL of THF, 7.7 mL (1.68M, 12.88 mmol) of *n*-BuLi in hexane was added dropwise at room temperature. A gradual change from a clear solution

to a white suspension was observed. After addition, the mixture was stirred overnight, the suspension was filtered and the remainder was dried under vacuum. THF (30 mL) and CH<sub>3</sub>I (1832 mg, 12.88 mmol) were added dropwise at -60°C, the mixture was warmed to r.t. slowly and stirred overnight. Then the solvent was evaporated, the residue was extracted with hexane (10 mL × 2) and dried under vacuum 877 mg of white powder [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>C<sub>5</sub>H<sub>3</sub>)<sub>2</sub>] were obtained with 50% yield.

To a solution of [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>C<sub>5</sub>H<sub>3</sub>)<sub>2</sub>] (877 mg, 3.22 mmol) in 50 mL of THF, 3.85 mL (1.68M, 6.44 mmol) of *n*-BuLi in hexane was added dropwise at room temperature. A gradually change from a clear solution to a white suspension was observed. After addition, the mixture was stirred overnight, the suspension was filtered and the residue was dried under vacuum. THF (40 mL) and ( $\eta^5$ -Cp)ZrCl<sub>3</sub>·DME (2272 mg, 6.44 mmol) were added at -60°C, the mixture was slowly warmed to r.t. and stirred overnight. Then the solvent was evaporated, the remainder was washed with hexane (10 mL × 2) and dried under vacuum, 1120 mg of white powder were obtained by crystallization from C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>/hexane in 48% yield (based on Zr). M.p. 213–214°C. <sup>1</sup>H NMR(CDCl<sub>3</sub>, 500 MHz):  $\delta$  6.62 (s, 2H, bridged-CpH), 6.54 (s, 2H, bridged-CpH), 6.32 (s, 10H, CpH), 2.14 (s, 6H, CpMeH), 0.51 (s, 12H, Me<sub>2</sub>Si); EI-MS (70 eV, *m/e*): 644(100, [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -CH<sub>3</sub>C<sub>5</sub>H<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>)ZrCl<sub>2</sub>)<sub>2</sub>), 346 (65, [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -CH<sub>3</sub>C<sub>5</sub>H<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>3</sub>)Zr]<sup>+</sup>); Anal. Calcd for C<sub>26</sub>H<sub>32</sub>Cl<sub>4</sub>Si<sub>2</sub>Zr<sub>2</sub>: C, 43.08; H, 4.45. Found: C, 42.74; H, 4.53.

#### Synthesis of [ $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)TiCl<sub>2</sub>]<sub>2</sub>[ $\mu$ , $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -allylC<sub>5</sub>H<sub>2</sub>)<sub>2</sub>] (2)

The synthetic procedure for 2 was the same as that for 1. [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>] (1.986g, 8.14 mmol); HC = CH<sub>2</sub>CH<sub>2</sub>Br (1969mg, 16.28 mmol); ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)TiCl<sub>3</sub> (1255mg, 5.70 mmol); 630 mg of dark red crystal was obtained in 32% yield (based on Ti). M.p. 208–210°C. <sup>1</sup>H-NMR(CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.17(s, 4H, bridged-CpH), 6.50 (s, 10H, CpH), 5.61–5.85 (m, 2H, = CH), 4.97–5.11 (m, 4H, = CH<sub>2</sub>), 3.34 (d, 4H, J = 6.0, CH<sub>2</sub>Cp), 0.53 (s, 12H, Me<sub>2</sub>Si). EI-MS (70 eV, *m/e*): 405(29, [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -allylC<sub>5</sub>H<sub>2</sub>)<sub>2</sub>TiCl]<sup>+</sup>), 365(100, [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -allylC<sub>5</sub>H<sub>2</sub>)(C<sub>5</sub>H<sub>2</sub>)TiCl]<sup>+</sup>), 329(45, [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -allylC<sub>5</sub>H<sub>2</sub>)(C<sub>5</sub>H<sub>2</sub>)Ti]<sup>+</sup>); Anal. Calcd for C<sub>30</sub>H<sub>36</sub>Cl<sub>4</sub>Si<sub>2</sub>Ti<sub>2</sub>: C, 52.20; H, 5.26. Found: C, 51.75; H, 5.17.

#### Synthesis of [ $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>2</sub>]<sub>2</sub>[ $\mu$ , $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -allylC<sub>5</sub>H<sub>2</sub>)<sub>2</sub>] (3)

The synthetic procedure for 3 was the same as that for 2. [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -allylC<sub>5</sub>H<sub>3</sub>)<sub>2</sub>] (1218 mg, 3.75 mmol); ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>3</sub>·DME (2653 mg, 7.51 mmol);

1648 mg of light white crystals were obtained in 56.5% yield (based on Zr). M.p. 224–226°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.02 (d, 4H, J = 2.5 Hz, bridged-CpH), 6.36 (s, 10H, CpH), 5.78–6.04 (m, 2H, = CH), 4.94–5.08 (m, 4H, = CH<sub>2</sub>), 3.37 (d, 4H, J = 6.4, CH<sub>2</sub>Cp), 0.52 (s, 12H, Me<sub>2</sub>Si); EI-MS (70 eV, *m/e*): 447(100, [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -allylC<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrCl]<sup>+</sup>), 432(38, [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)(MeSi)( $\eta^5$ -allylC<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrCl]<sup>+</sup>); Anal. Calcd for C<sub>30</sub>H<sub>36</sub>Cl<sub>4</sub>Si<sub>2</sub>Zr<sub>2</sub>: C, 46.37; H, 4.67. Found: C, 46.05; H, 4.51.

#### Synthesis of [ $(\eta^5$ -MeC<sub>5</sub>H<sub>4</sub>)ZrCl<sub>2</sub>]<sub>2</sub>[ $\mu$ , $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -allylC<sub>5</sub>H<sub>2</sub>)<sub>2</sub>] (4)

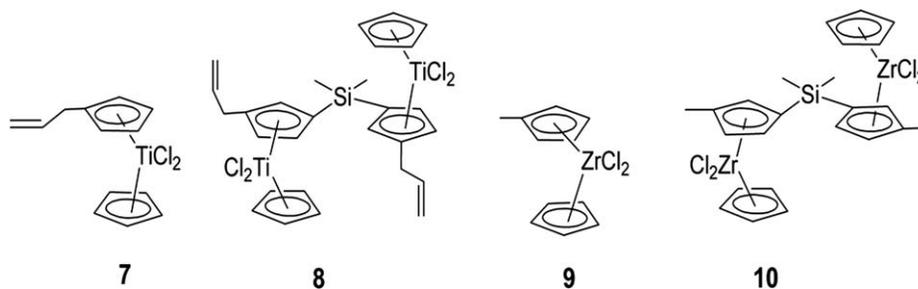
The synthetic procedure for 4 was the same as that for 3. [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -allylC<sub>5</sub>H<sub>3</sub>)<sub>2</sub>] (728 mg, 2.24 mmol); ( $\eta^5$ -CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)ZrCl<sub>3</sub>·DME (1644 mg, 4.48 mmol); 668 mg of white crystals were obtained in 37% yield (based on Zr). M.p. 218–220°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.01 (d, 4H, J = 2.6 Hz, bridged-CpH), 6.42 (d, 4H, J = 2.6 Hz, CpH), 6.18 (d, 4H, J = 2.7 Hz, CpH), 5.93 (m, 2H, = CH), 5.01 (m, 4H, = CH<sub>2</sub>), 3.39 (d, 4H, J = 6.4, CH<sub>2</sub>Cp), 2.24(s, 6H, CpCH<sub>3</sub>), 0.51(s, 12H, Me<sub>2</sub>Si). EI-MS (70 eV, *m/e*): 447 (56, [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -allylC<sub>5</sub>H<sub>2</sub>)<sub>2</sub>ZrCl]<sup>+</sup>), 406 (100, [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -allylC<sub>5</sub>H<sub>3</sub>)(C<sub>5</sub>H<sub>2</sub>)ZrCl]<sup>+</sup>); Anal. Calcd for C<sub>32</sub>H<sub>40</sub>Cl<sub>4</sub>Si<sub>2</sub>Zr<sub>2</sub>: C, 47.74; H, 5.01. Found: C, 47.55; H, 4.82.

#### Synthesis of [ $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)TiCl<sub>2</sub>]<sub>2</sub>[ $\mu$ , $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -<sup>n</sup>BuC<sub>5</sub>H<sub>2</sub>)<sub>2</sub>] (5)

The synthetic procedure for 5 was the same as that for 1. [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>] (1.63g, 6.70 mmol); CH<sub>3</sub>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br (1900 mg, 13.9 mmol); ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)TiCl<sub>3</sub> (2010 mg, 9.16 mmol); 1.15 g of dark red crystals were obtained in 36% yield (based on Ti). M.p. 224–227°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  6.91 (s, 4H, bridged-CpH), 6.59 (s, 10H, CpH), 1.57–1.53 (m, 4H, CH<sub>2</sub>Cp), 0.98–0.87 (m, 4H, CH<sub>2</sub>), 0.62–0.60 (m, 4H, CH<sub>2</sub>CH<sub>3</sub>), 0.55–0.52 (m, 6H, CH<sub>3</sub>), 0.49 (s, 12H, Me<sub>2</sub>Si); EI-MS (70 eV, *m/e*): 472(100, [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -<sup>n</sup>BuC<sub>5</sub>H<sub>2</sub>)<sub>2</sub>TiCl<sub>2</sub>]<sup>+</sup>), 437(41, [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -<sup>n</sup>BuC<sub>5</sub>H<sub>2</sub>)<sub>2</sub>TiCl]<sup>+</sup>), 402(5, [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -<sup>n</sup>BuC<sub>5</sub>H<sub>2</sub>)<sub>2</sub>Ti]<sup>+</sup>). Anal. Calcd for C<sub>32</sub>H<sub>44</sub>Cl<sub>4</sub>Si<sub>2</sub>Ti<sub>2</sub>: C, 53.20; H, 6.14. Found: C, 52.79; H, 6.09.

#### Synthesis of [ $(\eta^5$ -C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>2</sub>]<sub>2</sub>[ $\mu$ , $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>( $\eta^5$ -Me<sub>3</sub>SiC<sub>5</sub>H<sub>2</sub>)<sub>2</sub>] (6)

The synthetic procedure for 6 was the same as that for 1. [ $\mu$ ,  $\mu$ -(SiMe<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>] (641 mg, 2.63 mmol); Me<sub>3</sub>SiCl(570 mg, 5.26 mmol)65307( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)ZrCl<sub>3</sub>·DME (1.478 g, 4.20 mmol); 830 mg of light yellow crystals were obtained in 47% yield (based on Zr). M.p. 230–233°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.12 (d, 2H, J = 2.0 Hz, bridged-CpH), 7.01 (d, 2H, J =



**Chart 1** Earlier parent complexes mononuclear and mono-silylene-bridged binuclear complexes.

2.0 Hz, bridged-CpH), 6.40 (d, 10H,  $J = 5.0$  Hz, CpH), 0.51 (s, 12H,  $\text{Me}_2\text{Si}$ ), 0.32 (s, 18H,  $\text{Me}_3\text{Si}$ ), EI-MS (70 eV, m/e): 763 (100,  $[\text{M}-\text{Me}_3\text{Si}]^+$ ), 440 (80,  $[\mu-(\text{SiMe}_2)_2(\eta^5-\text{Me}_3\text{SiC}_5\text{H}_2)(\eta^5-\text{C}_5\text{H}_2)\text{ZrCl}]^+$ ); Anal. Calcd for  $\text{C}_{30}\text{H}_{44}\text{Cl}_4\text{Si}_2\text{Zr}_2$ : C, 45.89; H, 5.65. Found: C, 45.81; H, 5.54.

### Homogeneous polymerization procedure

Polymerizations were carried out in a Glove box. A 250-mL three-necked flask equipped with a magnetic stirrer was heated at  $100^\circ\text{C}$  under vacuum for 30 min and then cooled to the desired temperature by immersing into a thermostatically heated bath. The proper amount of MAO solution (additional 2.0 mL 1-hexene was added when copolymerization carried out), toluene solution of complex and more toluene to bring the final volume to 150 mL were added to the flask in that sequence and the reactor was pressurized with predried ethylene. The pressure was kept constant during the polymerization. The reaction mixture was stirred vigorously for a certain time. Totally, 15 mL of 10% HCl in ethanol was added to quench the polymerization. The contents of the flask were transferred to a beaker and then separated from the solution by filtration. The collected polymer was washed to neutral with ethanol and then dried overnight in a vacuum oven at  $60^\circ\text{C}$  to constant weight.

### CONCLUSIONS

We synthesized novel double  $\text{Me}_2\text{Si}$ -bridged binuclear complexes and examined their catalytic activity for ethylene polymerization and copolymerization with 1-hexene in present of MAO. We found that the nature of the substituents of different nature on the bridged-Cp ring plays an important role in the catalytic performance of this series of complexes. Among them, the **3/MAO** system exhibits the highest catalytic activity for homogeneous ethylene polymerization. The double  $\text{Me}_2\text{Si}$  bridged-Cp rings stabilized two activated metal centers and promoted

polymerization activity and the cooperative effect between the two metal centers broaden resulting polymer MWD. The "open structure" caused by freezing the metal configuration lead to increased comonomer content.

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