

Asymmetric Binuclear Metallocene Complexes and Their Application for Olefin Polymerization

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ABSTRACT: Asymmetric double silylene-bridged binuclear complexes $[(\eta^5\text{-RC}_5\text{H}_4)\text{MCl}_2]_2[\mu, \mu\text{-}(\text{SiMe}_2)_2(\eta^5\text{-t-BuC}_5\text{H}_2)(\eta^5\text{-C}_5\text{H}_3)]$ [R = H, M = Ti (1); R = Me, M = Ti (2); R = allyl, M = Ti(3); R = H, M = Zr (4); R = allyl, M = Zr (6)]; and $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_2]_2[\mu, \mu\text{-}(\text{SiMe}_2)_2(\eta^5\text{-Me}_3\text{SiC}_5\text{H}_2)(\eta^5\text{-C}_5\text{H}_3)]$ (5) were synthesized by the reaction of $(\eta^5\text{-RC}_5\text{H}_4)\text{TiCl}_3$ or $(\eta^5\text{-RC}_5\text{H}_4)\text{ZrCl}_3\cdot\text{DME}$ (R = H, allyl) with $[\mu, \mu\text{-}(\text{SiMe}_2)_2(\eta^5\text{-t-BuC}_5\text{H}_2)(\eta^5\text{-C}_5\text{H}_3)]\text{Li}_2$ or $[\mu, \mu\text{-}(\text{SiMe}_2)_2(\eta^5\text{-Me}_3\text{SiC}_5\text{H}_2)(\eta^5\text{-C}_5\text{H}_3)]\text{Li}_2$ in THF, and they were all well characterized by ^1H NMR, MS, IR, and EA. When activated with methylaluminoxane (MAO), they are efficient catalysts for the polymerization of ethylene (Complex 4, 5.99×10^5 g-PE/mol-Zr-h) and the polymer with multippeak broaden molecular weight distribution (PD = M_w/M_n) was obtained (polymer sample gained by complex 3, PD = 25.03). The copolymerization results indicate that 1-hexene could incorporate into the growing PE chain with these complexes in the presence of MAO (Complex 4, 1.07×10^6 g-PE/mol-Zr-h; 1-hexene content, 1.57% mol). © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

It is well known that numerous metallocene have been synthesized and used as efficient catalysts for the polymerization of olefin. Actually, the PD of resulting polymer from metallocene is very narrow ($M_w/M_n = 2\text{--}3$), which causes many trouble on the processability because of the high shear viscosity and low melt extensional viscosity.¹ To overcome this disadvantage, binuclear metallocene catalysts have been developed. Recently, Sun^{2–6} synthesized diphenyl bridged dinuclear titanocenes and used as catalyst for ethylene polymerization and PE with broad PD was obtained (PD = 7.56). However, most binuclear metallocene with single-bridge did not offer the opportunity to cooperative chemical behavior, because of the relative orientation between the two metal centers may vary in a flexible manner from of the rotation about the E-Cp bond (E = bridge atom). So the double-bridged binuclear complexes have been developed for increasing the stereo rigidity of the complexes. Royo and coworkers^{7,8} synthesized trans trichloride binuclear titanium complexes in 1994 and studied the structure by X-ray diffraction. Corey et al.^{9,10} also synthesized a series of such type of dichloride complexes and found that most of them are trans configuration. Lang¹¹ discovered that these titanium complexes

suit to polymerize ethylene with high activity under low ratio of Al/Ti ($P_{\text{ethylene}} = 10$ bar, $T = 50^\circ\text{C}$, $t = 2.0$ h, Al/Ti = 290, Act. = 3.0×10^5 g-PE/ mol-Ti-h). In 2002, Wang and coworkers¹² reported the effective polymerization of ethylene with mixed-bridged binuclear metallocene complexes (E = Ge, R = H, $P_{\text{ethylene}} = 1.0$ bar, $T = 40^\circ\text{C}$, $t = 0.5$ h, Al/Zr = 2500, Act. = 3.94×10^6 g-PE/mol-Zr h) and then discussed the effects of the bridges on the catalytic activities.¹³ In 2005, Hou¹⁴ developed novel special binuclear rare earth metal complexes and use it as catalyst for 3, 4-polymerization of isoprene. Mizuta¹⁵ synthesized bi- and trinuclear complexes of Group 4 metal, and found them showing high catalytic activities in double hydrophosphinylation of 1-octyne. In 2010 Wang and coworkers¹⁶ developed the amido-bridged zirconocene and studied their reactivity and catalytic behavior for ethylene polymerization, they found that the product existed mainly in the form of Al(PE)₃ with polymeric chains, and its molecular weight and distribution were greatly influenced by the type and amount of trialkylaluminium applied in the catalytic system. In 2011, Nie and coworkers^{17,18} synthesized dinuclear zirconocene complex bridged with phenyl sulfide and thioether, respectively. Now, more and more binuclear even trinuclear Group IV complexes¹⁹

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were synthesized, Ma and coworkers²⁰ developed binuclear heteroligand titanium catalyst based on phenoxyimine ligands and used for ethylene copolymerization with α -olefin, Ivanchev et al.²¹ synthesized binuclear phenoxyimine titanium halide complexes and used for ethylene polymerization. Recently, the binuclear zirconium complexes with bidentate N-(ortho-dimethylaminobenzyl)anilide ligand were prepared by Liu et al.,²² when activated with Al(*i*-Bu)₃ and Ph₃CB(C₆F₅)₄, these complexes produced ultra-high molecular weight polyethylene or relatively high molecular weight poly(ethylene-*co*-1-hexene) with reasonable 1-hexene incorporation. Lee et al.²³ reported a biphenylene-bridged dinuclear constrained geometry titanium complex for ethylene and ethylene/1-octene polymerizations and found this catalytic system exhibits significantly increased molecular weight, as well as high activity and high 1-octene incorporation in ethylene and ethylene/1-octene polymerizations in comparison with the corresponding mononuclear CGC analogs. In 2012, Lee²⁴ synthesized zirconium complexes containing fully deprotonated 2-(2H-benzo[d][1,2,3] triazol-2-yl) -4,6-di-*tert*-pentylphenol and used as catalysts for the polymerization of ethylene with controlled bimodal molecular weight distribution. Nohn group²⁵ induced the control of both molecular weight and comonomer response of ethylene polymerization via utilization of alkyl branches at the para-xylene bridge of new dinuclear constrained geometry catalysts. Wang et al.²⁶ synthesized the (R)-cyclopentadienyl-binaphthoxy titanium(IV) complexes and used for ethylene/1-hexene copolymerization and found that the high comonomer contents exhibit optical activity.

In the last decade, our group^{27–29} found that single-bridged/double-bridged hetero-binuclear or homo-binuclear titanium complexes with different substituted Cp ring gave excellent results on the olefin polymerization. In order to increase the stereo rigidity of the complexes, we³⁰ have designed and synthesized binuclear zirconium complexes with double silylene-bridge and introduced a series of different substituents on Cp ring, and studied their catalytic behavior for ethylene polymerization and ethylene/1-hexene copolymerization in the presence of MAO. It is found that all the binuclear zirconium complexes are effective catalysts not only for ethylene polymerization even under low ratio of Al/Zr (5.41×10^5 g-PE/mol-Zr-h, Al/Zr = 50), but also for ethylene/1-hexene copolymerization (3.59×10^6 g-PE/mol-Zr-h; 1-hexene content, 3.65% mol); polymers with broader PD ($M_w/M_n = 7.31–27.6$) were obtained. The said results suggest that the catalyst design must be focused on maximizing difference of chemical and stereo surroundings between the two homo-metal centers in one catalyst molecule.

However, to our best knowledge there are few articles about asymmetric binuclear complexes with double silylene-bridged. Now, in order to study the effect of the difference of chemical and stereo surrounding between the two homo-metal centers in one molecule on catalytic activity and polymer properties, we designed and synthesized a series of novel asymmetric double silylene-bridged binuclear complexes by introducing substituent on one side bridged Cp ring. The result shows that all the binuclear complexes are effective catalysts not only for ethylene polymerization, but also for ethylene/1-hexene copolymerization; polymers with multipeak PD was also obtained.

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 P₂O₅ under argon. Ethylene for polymerization was used after passing it through 4Å molecular sieves. 1-Hexene was distilled over sodium under argon and stored in the presence of activated 4Å molecular sieves. MAO was purchased from AZO Company. The CpTiCl₃ and (η^5 -RC₅H₄)ZrCl₃·DME were synthesized from the reaction of (RC₅H₄)SiMe₃ with MCl₄ according to the literature.³¹ Ligand [μ , μ -(SiMe₂)₂(C₅H₄)₂] and Li₂[μ , μ -(SiMe₂)₂(η^5 -C₅H₃)₂] were synthesized by the procedure described by Huhmann.⁹

IR spectra were recorded on a Nicolet MAGNA-IR 550 spectrometer as KBr pellets. ¹H-NMR spectra and ¹³C-NMR were recorded on a Bruker ADVANCE DMX 500 spectrometer in CDCl₃ (for complexes 1–5) and *o*-C₆D₄Cl₂ (for polymer samples). 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 and polystyrene was used as a standard.

Synthesis of [μ , μ -(SiMe₂)₂(*t*-BuC₅H₃)(C₅H₄)] (Ligand I)

To a solution of 6,6-dimethylfulvene (16.0 g, 0.15 mol) in diethyl ether (100 mL), MeLi (100 mL, 1.50M, 0.15 mol) in hexane was added dropwise at room temperature (r.t.) and a gradual change from clear solution to white suspension was observed. After addition, the mixture was stirred overnight and filtered, then the residue was dissolved in THF (100 mL) and the light yellow clear solution of *t*-BuCpLi was obtained.

A solution of (C₅H₅)SiMe₂Cl (23.4 g, 0.15 mol) in THF (20 mL) and diethyl ether (30 mL) was slowly added dropwise to the solution of *t*-BuCpLi at r.t. and the mixture was stirred overnight and treated with 1.0M HCl solution until the pH = 2–3, then the organic phase was separated and washed with water until pH = 7, dried with anhydrous MgSO₄ and light yellow liquid product *t*-BuC₅H₄(Me₂)SiC₅H₅ (35.0 g, 90% yield) was obtained after the solvent removed.

To the solution of *t*-BuC₅H₄Si(Me₂)C₅H₅ (17.0 g, 85 mmol) in THF (20 mL) and diethyl ether (100 mL), *n*-BuLi (90 mL, 1.8 M, 171 mmol) was added dropwise at r.t. and stirred overnight. Then the solvent was removed under vacuum and the solid Li₂[*t*-BuC₅H₃Si(Me₂)C₅H₄] was washed with *n*-hexane until the white powder was gained, then dissolved in THF (100 mL) and Me₂SiCl₂ (10.0 mL) was added at –78°C, the mixture was slowly warmed to r.t. and stirred for 2 days. Then the liquid organic phase was concentrated and light yellow crystal Ligand I (7.35 g, 31.36% yield) was obtained.

Synthesis of Ligand II

It is well known that numerous mononuclear metallocene with asymmetric double Me₂Si-bridge have been reported in Ref. 7. In 1993, Brintzinger and coworkers³² reported a synthetic route for asymmetric double-bridged cyclopentadienyl rings with different substituents by cyclization of asymmetric single-bridge

cyclopentadienyl rings. In 1995, Lang¹¹ introduced another synthetic road for asymmetric double-Me₂Si-bridged bicyclopentadiene by introducing substituent on one side of double-bridged bicyclopentadienyl ring. It is obvious that Lang's synthetic route is simple so we synthesized Ligand II [μ , μ -(Me₂Si)₂(Me₃SiC₅H₃)(C₅H₄)] according to Lang's route.

Synthesis of [η^5 -C₅H₅TiCl₂]₂ [μ , μ -(SiMe₂)₂(η^5 -*t*-BuC₅H₂)(η^5 -C₅H₃)] Complex 1

To a solution of Ligand I (1.033 g, 3.44 mmol) in *n*-hexane (20 mL), *n*-BuLi (4.50 mL, 6.88 mmol, 1.53M) in hexane was added dropwise at r.t. and a gradual change from clear solution to white suspension was observed. After addition, the mixture was stirred overnight and CpTiCl₃ (0.811 g, 6.89 mmol) in THF (20 mL) were added at -50°C, the mixture was slowly warmed to 40°C and stirred overnight and a deep red suspension was obtained. Then the liquid phase was obtained by filter and the residue was extracted with CH₂Cl₂ (10 mL × 2), the filtrate and extractive CH₂Cl₂ was combined and the solvent was evaporated, deep red crystals were obtained by recrystallization from CH₂Cl₂/hexane (1.55 g, 68.9% yield based on Ti). M.P. 168°C. ¹H NMR(500 MHz, CDCl₃, δ , ppm) : 0.49(d, *J* = 9.7 Hz, 12 H, 2 × (CH₃)₂Si), 1.29(s, 9 H, (CH₃)₃C-Cp bridged), 6.48(s, 5 H, nonbridged C₅H₅), 6.56(s, 5 H, nonbridged C₅H₅), 6.72(t, *J* = 2.20 Hz, 1H, bridged C₅H₃), 7.14(d, *J* = 2.20 Hz, 2 H, bridged C₅H₃), 7.07(s, H, bridged *t*-BuC₅H₂), 7.03(s, 1 H, bridged *t*-BuC₅H₂). I.R. (KBr, thin film, cm⁻¹): 3530 w, 3105 w, 3083 w, 2959 w, 2897 w, 2868 w, 1460 w, 1442 w, 1396 w, 1365 w, 1244 m, 1199 m, 1098 w, 1057 w, 1017 w, 981 w, 957 w, 814 s, 779 s, 677 m, 602 w, 512 w, 465 w, 428 w. EI-MS (m/e) : 482(8, [μ , μ -(SiMe₂)₂(*t*-BuC₅H₂)(C₅H₃)(CpTiCl₂)]⁺), 461(16, [μ , μ -(SiMe₂)₂(SiMe)(C₅H₃)(TiCl₂)]⁺), 360(34, [μ , μ -(SiMe₂)₂(C₅H₃)₂TiCl₂]⁺), 325([μ , μ -(SiMe₂)₂(C₅H₃)₂TiCl]⁺), 290(100, [μ , μ -(SiMe₂)₂(C₅H₃)₂]⁺), 183(63, [CpTiCl]⁺), 148(45, [CpTi]⁺). Anal. calcd. for C₂₈H₃₆Cl₄Si₂Ti₂: C 50.47%; H 5.45%. Found: C 49.87%; H 5.22%.

Synthesis of [η^5 -MeCpTiCl₂]₂ [μ , μ -(SiMe₂)₂(η^5 -*t*-BuC₅H₂)(η^5 -C₅H₃)] Complex 2

Synthetic procedure for complex 2 was the same as that for complex 1. Ligand I (1.065 g, 3.55 mmol); *n*-BuLi (5.50 mL, 1.28M, 7.04 mmol); MeCpTiCl₃ (1.615 g, 6.926 mmol) deep red crystal was obtained (1.62 g, 65.7% yield based on Ti). M.P. 183°C. ¹H NMR(500 Mz, CDCl₃, δ , ppm) : 0.48(d, *J* = 9.6 Hz, 12 H, 2 × (CH₃)₂Si), 1.27 (s, 9 H, (CH₃)₃C-Cp), 2.28(s, 3 H, CH₃Cp), 2.33(s, 3 H, CH₃Cp), 6.13(t, *J* = 3.0 Hz, 4 H, MeC₅H₄), 6.36–6.37(m, 4 H, MeC₅H₄), 6.51(t, *J* = 2.4 Hz, 2 H, bridged C₅H₃), 7.05(s, 1 H, bridged C₅H₃), 7.11(d, *J* = 2.3 Hz, 1 H, bridged *t*-BuC₅H₂), 7.14(d, *J* = 2.3 Hz, 1H, bridged *t*-BuC₅H₂); I.R. (KBr, thin film, cm⁻¹) : 3427 w, 3120 w, 3101 w, 2961 w, 2925 w, 2895 w, 2865 w, 1497 w, 1458 w, 1398 w, 1365 w, 1243 m, 1210 m, 1196 m, 1091 w, 1054 w, 1040 w, 980 w, 981w, 959 w, 944 w, 903 w, 841 s, 816 s, 780 s, 743 w, 679 m, 604 w, 513 m, 495 w, 466 w, 427 w. EI-MS (m/e) : 416(52, [μ , μ -(SiMe₂)₂(*t*-BuC₅H₂)(C₅H₃)TiCl₂]⁺), 381(100, [μ , μ -(SiMe₂)₂(*t*-BuC₅H₂)(C₅H₃)TiCl]⁺), 330(50, [μ , μ -(SiMe₂)₂(CH₂=C(Me)C₅H₂)(C₅H₃)Ti]⁺), 197(70, [MeCpTiCl₂]⁺), 162(58, [MeCpTiCl]⁺). Anal. Calcd. for C₃₀H₄₀Cl₄Si₂Ti₂: C 51.89%; H 5.81%. Found : C 51.89%; H 5.68%.

Synthesis of [η^5 -allylCpTiCl₂]₂ [μ , μ -(SiMe₂)₂(η^5 -*t*-BuC₅H₂)(η^5 -C₅H₃)] Complex 3

Synthetic procedure for complex 3 was the same as that for complex 1. Ligand I (0.628 g, 2.095 mmol); *n*-BuLi (3.30 mL, 1.28M, 4.186 mmol); allylCpTiCl₃ (1.084 g, 4.186 mmol). Deep red crystal was obtained (1.32 g, 85% yield based on Ti). M.P. : 206 °C. ¹H NMR(500 Mz, CDCl₃, δ , ppm) : 0.47(d, *J* = 9.2 Hz, 12 H, 2 × (CH₃)₂Si), 1.27 (s, 9 H, (CH₃)₃C-Cp), 3.45 (d, *J* = 6.6 Hz, 2 H, CH₂Cp), 3.50 (d, *J* = 6.6 Hz, 2 H, CH₂Cp), 4.99–5.04 (m, 4 H, CH₂=), 5.86–5.96 (m, 2 H, =CH-), 6.20 (d, *J* = 2.8 Hz, 4 H, nonbridged C₅H₄), 6.38 (t, *J* = 2.4 Hz, 2 H, nonbridged C₅H₄), 7.12 (d, *J* = 2.4 Hz, 2 H, nonbridged C₅H₄), 6.36 (s, 1 H, Bridged C₅H₃), 6.53 (t, *J* = 2.50 Hz, 2 H, Bridged C₅H₃), 7.06(s, 2H, *t*-BuC₅H₂). I.R. (KBr, cm⁻¹) : 3431 w, 3120 w, 3096 w, 2960 w, 2897 w, 1655 w, 1636 w, 1490 w, 1460 w, 1429 w, 1407 w, 1365 w, 1245 m, 1208 w, 1197 w, 1094 w, 1052 w, 1036 w, 989 w, 958 w, 910 w, 838 s, 817 s, 776 m, 742 w, 677 w, 604 w, 512 w, 495 w, 467 w, 427 w. EI-MS(m/e) : 744(1, M⁺), 416 [μ , μ -(SiMe₂)₂(*t*-BuC₅H₂)(C₅H₄)Ti Cl₂]⁺, 381(100, [μ , μ -(SiMe₂)₂(*t*-BuC₅H₂)(C₅H₄)Ti Cl]⁺), 330(30, [μ , μ -(SiMe₂)₂(CH₂=C(Me)C₅H₃)(C₅H₄)Ti]⁺), 187(4, [allylCp-TiCl]⁺). Anal. Calcd. for C₃₄H₄₄Cl₄Si₂Ti₂: C 54.71%; H = 5.94%. Found: C 54.88%; H = 6.22%.

Synthesis of [η^5 -CpZrCl₂]₂ [μ , μ -(SiMe₂)₂(η^5 -*t*-BuC₅H₂)(η^5 -C₅H₄)] Complex 4

Synthetic procedure for complex 4 was the same as that for complex 1. Ligand I (1.03 g, 3.48 mmol); *n*-BuLi (4.50 mL, 1.58M, 7.11 mmol); CpZrCl₃·DME(2.43 g, 6.89 mmol), white powder was obtained (0.86 g, 33% yield based on Zr). M.P. : 232°C. ¹H NMR (500 Mz, CDCl₃, δ , ppm) : 0.52(d, *J* = 2.8 Hz, 12 H, 2 × (CH₃)₂Si), 1.34(s, 9 H, (CH₃)₃C-Cp bridged), 6.41(s, 5 H, nonbridged C₅H₅), 6.46(s, 5 H, nonbridged C₅H₅), 6.50(t, *J* = 2.6 Hz, 1 H, bridged C₅H₃), 6.93(s, 2 H, bridged *t*-BuC₅H₂), 7.02(d, *J* = 2.6 Hz, 2 H, bridged C₅H₃). I.R. (KBr, thin film, cm⁻¹) : 3375 w, 3085 m, 2960 s, 2898 m, 1654 w, 1625 w, 1484 w, 1462 m, 1442 m, 1403 w, 1366 m, 1247 s, 1196 s, 1163 w, 1096 s, 1077 m, 1057 s, 1019 s, 992 m, 958 m, 920 w, 893 w, 869 w, 809 s, 779 s, 677 s, 606 w, 514 m, 466 m, 414 m. EI-MS(m/e) : 737(100, [μ , μ -(SiMe₂)₂(CH₂=C(Me)C₅H₂)(C₅H₃)(CpZrCl₂)₂]⁺), 428(38, [μ , μ -(SiMe₂)₂(*t*-BuC₅H₂)(C₅H₃)ZrCl]⁺), 407(45, [μ , μ -(SiMe₂)₂(CH₂=C(Me)C₅H₃)(C₅H₄)Zr Cl]⁺), 371(30, [μ , μ -(SiMe₂)₂(CH₂=C(Me)C₅H₃)(C₅H₄)Zr]⁺), 225(35, [CpZrCl₂]⁺). Anal. Calcd. for C₂₈H₃₆Cl₄Si₂Zr₂: C 44.66%; H 4.82%. Found : C 45.16%; H 5.03%.

Synthesis of [η^5 -CpTiCl₂]₂ [μ , μ -(SiMe₂)₂(η^5 -Me₃SiC₅H₂)(η^5 -C₅H₃)] Complex 5

To the solution of [μ , μ -(SiMe₂)₂(C₅H₄)₂]] (0.763 g, 3.12 mmol) in *n*-hexane(30 mL), *n*-BuLi (2.40 mL, 1.28M, 3.072 mmol) was added dropwise and the mixture was stirred overnight, then Me₃SiCl (3.01 mmol) was added and stirred overnight. The solvent was removed under vacuum and the residue was extracted by *n*-hexane(20 mL) and the solution of [μ , μ -(SiMe₂)₂(Me₃SiC₅H₃)(C₅H₄)] was obtained. To the solution, *n*-BuLi (4.80 mL, 1.28 M, 6.144 mmol) was added and the mixture was stirred overnight, then CpTiCl₃ (1.23 g, 5.63 mmol) in THF (20 mL) was added and the white suspension immediately turn into red. The mixture was stirred overnight. Then the



Scheme 1. Synthesis of asymmetric Ligand I.

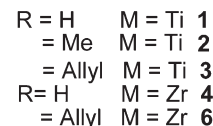
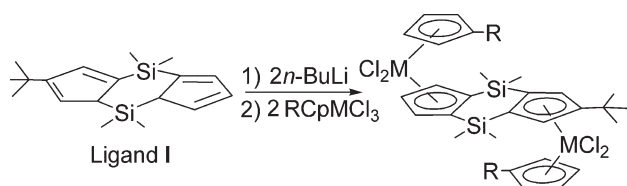
liquid phase was obtained by filter and the residue was extracted with CH_2Cl_2 (10 mL \times 2), the filtrate and extract CH_2Cl_2 was combined and the solvent was removed, deep red crystal (320 mg, 15% yield based on Ti) were obtained by recrystallization from CH_2Cl_2 /hexane. M.P. : 178°C. ^1H NMR (500 Mz, CDCl_3 , δ , ppm) : 0.49 (d, $J = 4.2$ Hz, 12H, $2 \times (\text{CH}_3)_2\text{Si}$), 0.30 (s, 9 H, $(\text{CH}_3)_3\text{Si-Cp}$), 6.50 (d, $J = 2.8$ Hz, 10 H, nonbridged C_5H_5), 6.40 (t, $J = 2.5$ Hz, 1 H, bridged C_5H_5), 7.27 (s, 2H, bridged $\text{Me}_3\text{Si-C}_5\text{H}_2$), 7.16 (d, 2H, $J = 2.5$ Hz, bridged C_5H_3). I.R. (KBr, cm^{-1}) : 3446 m, 3115 w, 2954 w, 2943 w, 1637 w, 1443 w, 1409 w, 1378 w, 1250 m, 1210 w, 1095 w, 1024 w, 955 w, 839 s, 818 s, 780 m, 679 w, 635 w, 540 w, 471 w, 430 w. EI-MS(m/e) : 679.98(m, 5), 432(29, $[\mu, \mu-(\text{SiMe}_2)_2(\text{Me}_3\text{SiC}_5\text{H}_2)(\text{C}_5\text{H}_3)]\text{TiCl}_2^+$), 397(100, $[\mu, \mu-(\text{SiMe}_2)_2(\text{Me}_3\text{SiC}_5\text{H}_2)(\text{C}_5\text{H}_3)]\text{TiCl}^+$), 182.92(78, $[\text{CpTiCl}_2]^+$), 147.95(52, $[\text{CpTiCl}]^+$), 362(54, $[\mu, \mu-(\text{SiMe}_2)_2(\text{Me}_3\text{SiC}_5\text{H}_2)(\text{C}_5\text{H}_3)]\text{Ti}^+$). E.A.: $\text{C}_{27}\text{H}_{36}\text{Cl}_4\text{Si}_3\text{Ti}_2$ Cal. HRMS, 679.9838 Found, 679.9790.

Synthesis of $[\eta^5\text{-allylCpZrCl}_2]_2[\mu, \mu-(\text{SiMe}_2)_2(\eta^5\text{-}^t\text{BuC}_5\text{H}_2)(\eta^5\text{-C}_5\text{H}_3)]$ Complex 6

Synthetic procedure for complex 6 was the same as that for complex 1. Ligand I (0.863 g, 2.88 mmol); *n*-BuLi (4.60 mL, 1.28M, 5.89 mmol); allylCpZrCl₃·DME (2.126 g, 5.42 mmol). White powder (56 mg, 2.5% yield) was obtained. M.P. : 242°C. ^1H NMR (500 Mz, CDCl_3 , δ , ppm) : 0.51(s, 12 H, $(\text{CH}_3)_2\text{Si}$), 1.32(s, 9 H, $(\text{CH}_3)_3\text{C-Cp}$), 6.29(s, 2H, nonbridged C_5H_4), 6.36(s, 2H, nonbridged C_5H_4), 6.12(s, 4H, nonbridged C_5H_4), 6.33(s, 1 H, bridged C_5H_2), 6.93(s, 1 H, bridged $^t\text{BuC}_5\text{H}_2$), 6.23(s, 1 H, bridged C_5H_3), 6.52(s, 1 H, bridged C_5H_3), 5.00–5.10(m, 4 H, $\text{H}_2\text{C}=\text{}$), 7.03(s, 1 H, bridged $^t\text{BuC}_5\text{H}_2$), 3.36–3.42(m, 4 H, $-\text{H}_2\text{C-Cp}$), 5.89–5.94(m, 2 H, $=\text{CH}$). I.R. (KBr, thin film, cm^{-1}) : 3370 w, 3095 m, 2970 s, 2888 m, 1647 w, 1422 m, 1366 m, 1250 s, 1200 s, 1066 s, 982 m, 928 m, 920 w, 893 w, 869 w, 829 s, 809 s, 779 s, 687 s, 514 m, 466 m, 414 m. EI-MS(m/e) : 761(84, $[\text{M}-2\text{HCl}]^+$), 367(100, $[\mu, \mu-(\text{SiMe}_2)_2(\text{C}_5\text{H}_2)(\text{C}_5\text{H}_3)]\text{ZrCl}^+$), 331(10, $[\mu, \mu-(\text{SiMe}_2)_2(\text{C}_5\text{H}_2)(\text{C}_5\text{H}_3)]\text{Zr}^+$), 265(16, $[\text{H}_2\text{C}=\text{CHCH}_2\text{C}_5\text{H}_4\text{ZrCl}_2]^+$), 229(17, $[\text{H}_2\text{C}=\text{CHCH}_2\text{C}_5\text{H}_4\text{ZrCl}]^+$). Anal. Calcd. for $\text{C}_{34}\text{H}_{44}\text{Cl}_4\text{Si}_2\text{Zr}_2$: C 50.01%; H 5.32%. Found: C 49.01%; H 5.28%.

Polymerization Procedure

A 100-mL autoclave equipped with a magnetic stirrer was heated at 110°C under vacuum for 30 min and then cooled to the desired temperature by immersing into a thermostatic bath. Proper amount of MAO solution, toluene solution of complex, and more toluene to bring the final volume to 25 mL were added to the autoclave 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 designed time and then vented. Ten



Scheme 2. Synthesis of asymmetric complexes 14 and 6.

milliliters of 5% HCl in ethanol was added to quench the polymerization. The contents of the reactor were transferred to a beaker and then the polymer was separated from the solution by filtration, washed to neutral with ethanol and then dried overnight in a vacuum oven at 60°C to constant weight.

Copolymerization Procedure

Copolymerization was carried out similarly to that for ethylene homopolymerization. A 100-mL autoclave, equipped with a magnetic stirrer bar, was heated at 110°C under vacuum for 30 min and then cooled to the required temperature. Toluene, 1-hexene, MAO, toluene solution of complex were injected into the reactor in that sequence, a proper amount of toluene was added to bring the final volume to 25 mL. The reactor was then pressurized with predried ethylene and the reaction mixture was stirred vigorously at desired temperature for a certain time. The treatment of copolymer was the same as that for polyethylene.

RESULTS AND DISCUSSION

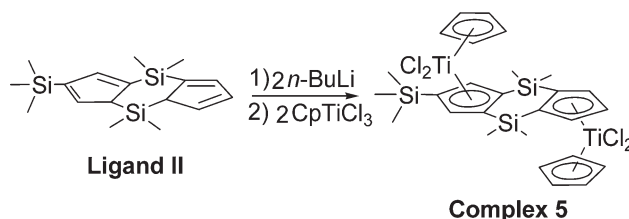
Synthesis and Characterization of Complexes 1–6

The novel asymmetrical double-bridged bicyclopentadienyl ring Ligand I $[\mu, \mu-(\text{Me}_2\text{Si})_2(t\text{-BuC}_5\text{H}_3)(\text{C}_5\text{H}_4)]$ was synthesized (shown in Scheme 1).

Ligand II $[\mu, \mu-(\text{Me}_2\text{Si})_2(\text{Me}_3\text{SiC}_5\text{H}_3)(\text{C}_5\text{H}_4)]$ was synthesized according to the literature.^{11,31} The general method to prepare complexes 1–4 and 6 was the reaction of two equiv. of $(\eta^5\text{-RC}_5\text{H}_4)\text{MCl}_3$ (M = Ti, Zr) with $\text{Li}_2[\mu, \mu-(\text{Me}_2\text{Si})_2(\eta^5\text{-}^t\text{BuC}_5\text{H}_2)(\eta^5\text{-C}_5\text{H}_3)]$ (from Ligand I) in THF (illustrated in Scheme 2).

Complex 5 was obtained via the reaction of two equiv. of $(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_3$ with $\text{Li}_2[\mu, \mu-(\text{Me}_2\text{Si})_2(\eta^5\text{-Me}_3\text{SiC}_5\text{H}_2)(\eta^5\text{-C}_5\text{H}_3)]$ in THF (see Scheme 3).

All the complexes are soluble in aromatic hydrocarbons (benzene, toluene), CH_2Cl_2 , and THF, scarcely soluble in diethyl ether, and insoluble in alkane. They are sensitive to air and



Scheme 3. Synthesis of asymmetric complex 5.

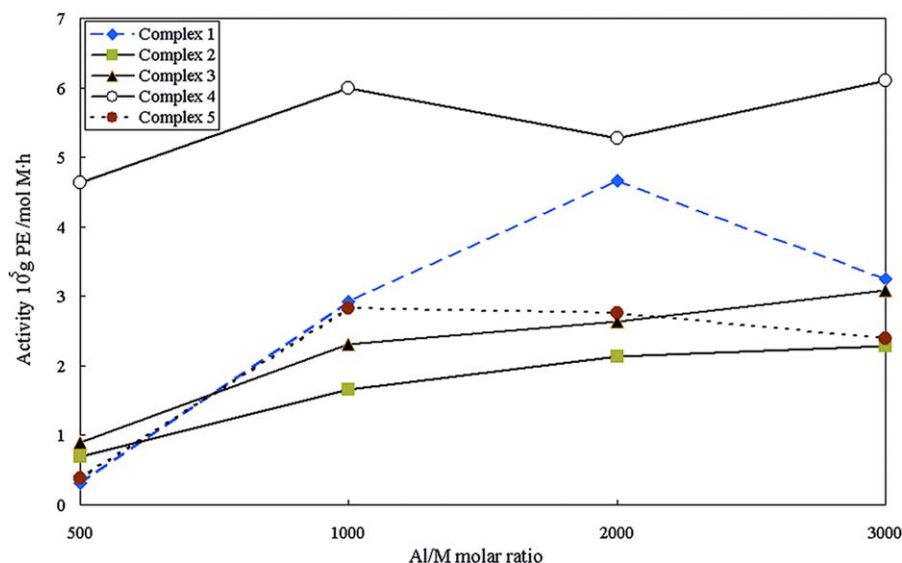


Figure 1. Influence of ratio of Al/M on activity. Condition: [Cat.] = 2.0 μmol , t = 30 min, T = 60°C, Total volume = 25 mL, P_{ethylene} = 1.0 MPa, Solvent = Toluene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

moisture. Complexes 1–5 were characterized by ^1H NMR, IR, Mass, and EA. Complex 6 was obtained with very low yield and not easy to purify, so EA amount was not satisfactory.

The symmetric double-bridged binuclear complexes³¹ are all *trans* configuration and the four silylene-bridging methyl groups are equivalent according to only one signal in ^1H NMR was found. But in the case of the asymmetric double-bridged binuclear complexes, four silylene-bridging methyl groups are not equivalent and could divide into two groups: the upper two Me_2Si methyl and the lower two Me_2Si methyl, so splitted signal in ^1H NMR of silylene-bridging methyl was observed for complexes 1–6, respectively, which was from the different surroundings because of *tert*-butyl introducing on one side of double-bridged Cp rings.

Ethylene Polymerization with Complexes 1–5

When activated with MAO, complexes 1–5 are effective catalyst for ethylene polymerization. From the ^{13}C NMR spectra of polyethylene samples, it was found that these polymers are linear mPEs without any branch chain indicated by the only singlet of $(\text{CH}_2)_2$ at $\delta = 29.9$, which means there are no branch chain and carbon–carbon double bond in polymer chain structure, we suggest that the chain termination did not fulfill by β -H elimination mechanism. The influence of factors such as reaction temperature, reaction time and molar ratio of Al/M on catalytic activity was also investigated.

The effect of cocatalyst MAO amount on catalytic activity and molecular weight were tested and the result was shown in Figures 1 and 2, respectively.

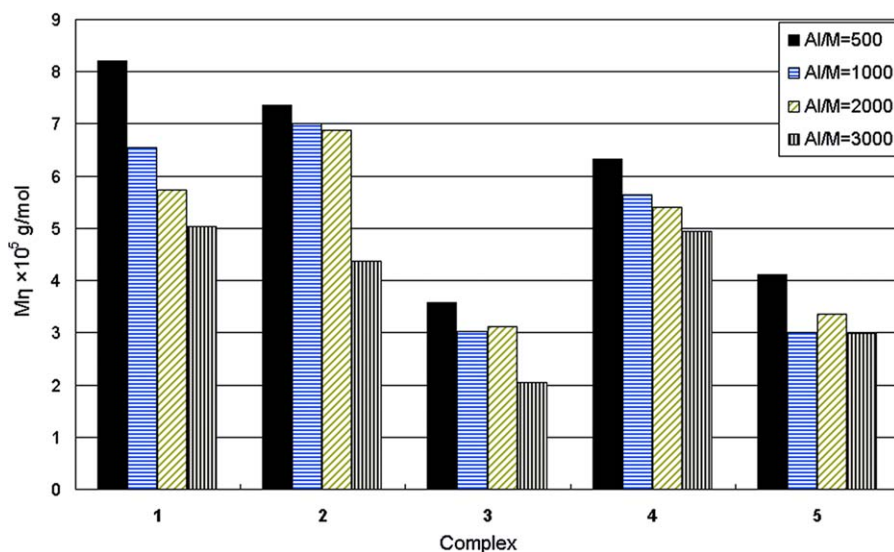


Figure 2. Effect of ratio of Al/M on molecular weight. Condition: [Cat.] = 2.0 μmol , t = 30 min, T = 60°C, Total volume = 25 mL, P_{ethylene} = 1.0 MPa, Solvent = Toluene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

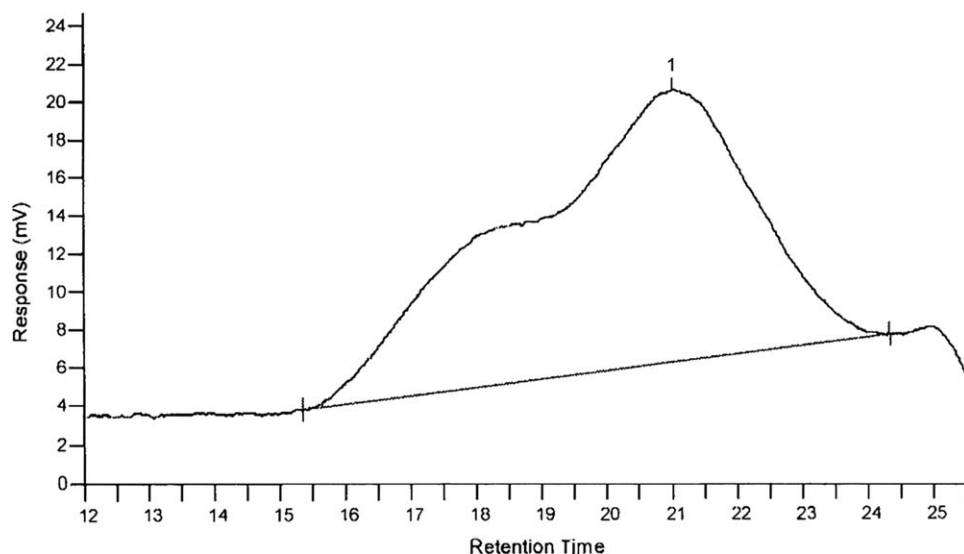


Figure 3. GPC trace of PE sample by complex 2. GPC was obtained on PL-GPC210 at 135°C and polystyrene used as standard.

From the result, it is found that the entire complexes are effective catalyst for ethylene polymerization in the presence of MAO and the zirconium complex 4 shows the highest activity. Among these titanium complexes, 1 (*t*-Bu, R = H, M = Ti) shows the highest activity, which we described from minimum steric bulkiness effect. From Figure 1, it is also found that the catalytic activity increases rapidly as the ratio of Al/M enhances from 500 to 1000 and later slowly raises as Al/M increases from 1000 to 3000, implying that for practical purpose Al/M molar ratio of about 1000 is ideal for the polymerization, just as the case we³⁰ found in symmetric binuclear complexes, any further increase will only have slight impact on the activity. Koltzenburg³³ found same phenomena and gave explanation: the reversible coordination of neutral MAO to the very Lewis-acidic metal cation $[(\eta^5\text{-Cp})_2\text{MMe}]^+$ reduced its electrophilicity, and such a reversibly coordination leads to less reactivity of metal cation, for example the MAO counterion, and the slower deactivation was observed at higher MAO concentration.

Compared with similar symmetric binuclear complex, asymmetric complexes have no activity under low ratio of Al/M (Al/Ti < 300 and Al/Zr < 100)^{29,30}, which we described to the decrease of cation stability because of asymmetric bridge fragment. It is also found that the activity of asymmetric binuclear complex (complex 1, Al/M = 500, $P_{\text{ethylene}} = 1.0$ MPa, 30 min, Act. = 0.315×10^5 g-PE/mol-Ti·h; complex 4, 4.63×10^5 g-PE/mol-Zr·h) is lower than that of symmetric double Me₂Si-bridged binuclear complex under same polymerization condition (3.03×10^5 g-PE/mol-Ti·h²⁹; 1.0×10^6 g-PE/mol-Zr·h³⁰, which we also ascribe to steric bulkiness effect because of asymmetric bridge fragment.

Figure 2 summarizes the result of the influence of Al/M ratio on the polymer molecular weight. From the result, it is found that the polymer molecular weight descends as the ratio of Al/M increases from 500 to 3000, which means the process of polymer chain transfer was easy happened at high ratio of Al/M.

It is noteworthy that despite the double-bridged fragment was symmetric or not, all of the mPEs obtained with these binuclear complexes have more higher molecular weights ($M_w = 1.28\text{--}6.03 \times 10^5$ g/mol²⁹; $M_w = 4.86\text{--}7.19 \times 10^5$ g/mol³⁰) than that of single sily-bridged binuclear complexes ($M_w = 0.93\text{--}1.24 \times 10^5$ g/mol^{27,29}). About this phenomena Marks and coworkers^{34–37} have given explanation, they studied the proximity effects in binuclear “constrained geometry catalysts (CGCs)” combined with the bifunctional bisborane activator and found that the obtained polymer molecular weight (M_n) was higher than that of mononuclear metallocene complex without cooperativity effects. This cooperative behavior explains the increased polymer molecular weights observed, in good agreement with experiment.

The GPC analysis results of PE samples ([Cat.] = 2.0 μmol; $t = 30$ min, $P_{\text{ethylene}} = 1.0$ MPa, $T = 60^\circ\text{C}$, Al/M = 1000) obtained from complexes 1–5 are carried out and the GPC curve of the PE from Complex 2 is shown in Figure 3.

From the result of GPC, it is found that the average molecular weight of the mPEs samples generated by complex 1 ($M_w = 237,724$, PD = 8.16), 2 ($M_w = 130,352$, PD = 10.35) and 4 ($M_w = 179,822$, PD = 4.95) is analogical from those obtained by the similar symmetric binuclear complexes.^{29,30} The molecular weights ($M_w = 1.30 \times 10^5\text{--}2.37 \times 10^5$) are much higher, which means low rate of chain termination. We ascribe the result from the different electronic environment of the metal sites because of the double-bridged Cp Ligands. We know well that the substituted group on nonbridged Cp ring affected the polymer molecular weight significantly, now the molecular weights increase in the order: 3 (allyl, M = Ti, $M_w = 60,098$) < 2 (Me, M = Ti, $M_w = 130,352$) < 1 (H, M = Ti, $M_w = 237,724$). On other hand, substituted group on double-bridged Cp rings also influenced the polymer molecular weight with same rule: 5 (Me₃Si, R = H, M = Ti, $M_w = 66,151$, PD = 17.6) < 1 (*t*-Bu, R = H, M = Ti, $M_w = 237,724$, PD = 8.16),

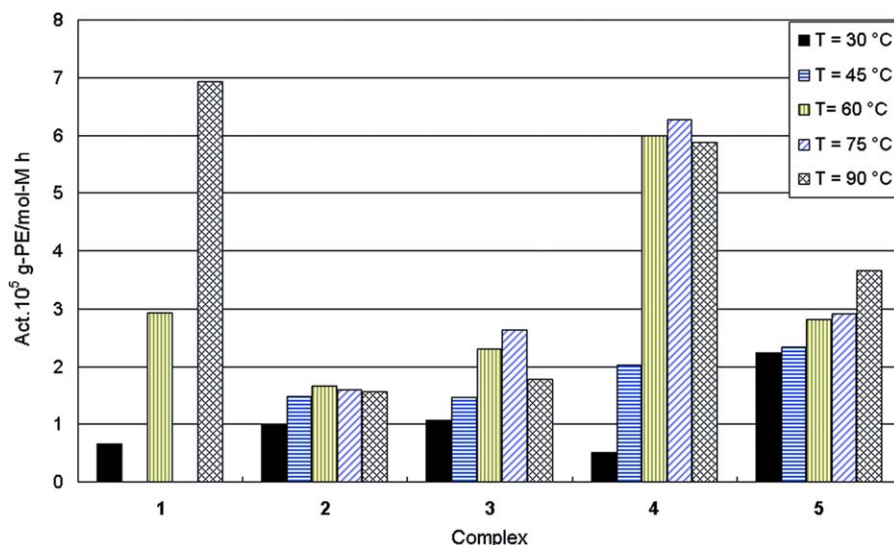


Figure 4. Effect of temperature on catalytic activity of ethylene polymerization. Condition: [Cat.] = 2.0 μmol , Al/M = 1000:1, t = 30 min, Total volume = 25 mL, P_{ethylene} = 1.0 MPa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

both of the above results imply the steric bulkiness of the substituent affects the rate of chain termination and the molecular weight decline as the group's bulkiness increases. The polymer we obtained has been characterized with ^1H NMR and ^{13}C NMR. However, the signals of carbon-carbon double bond have not been detected in the result of ^1H NMR and ^{13}C NMR, that is, the chain-end-group of the polyethylene's is not vinyl $\text{C}=\text{C}$, which implies that the mechanism of chain termination mechanism was not β -H elimination in our applied condition. Chen and coworkers^{16,38,39} found that chain transfer to Aluminium in MAO-activated metallocene-catalyzed polymerization reactions and the polymer chain was obtained without carbon-carbon double bond as chain-end-group especially when large steric bulkiness metallocene was used. Our result was similar to that of Chen.

It is noteworthy that the values of PD of titanium complexes increase in the order: 1 (t -Bu, H, PD = 8.16) < 2 (t -Bu, Me, PD = 10.35) < 3 (t -Bu, allyl, PD = 25.03), which we owe to the enlargement of difference between the two metal centers as the group's bulkiness augment. On the other hand we observed that the zirconium complex 4 (t -Bu, H, PD = 4.95) exhibited highest catalytic activity with the smallest PD. We suggested that, compared with titanium complex, the activity of zirconium complex 4 is much higher, which means the similar chemical surroundings have few effect on zirconium center than that of titanium. We also found the GPC curves of the samples by complex 2 is clearly made up of multipeak, which allows assuming that there is more than one active site during the polymerization process. Furthermore, the result confirms our initial idea: the control of catalytic behavior could be achieved by creating diverse chemistry surrounding on the two metal atoms in homo-binuclear complex and polymer with multipeak PD could be gained by these complexes.

The result of the temperature on activity is shown in Figure 4.

It is obvious that all complexes kept high activity even at 90°C, which implies that these complexes are stable under higher temperature. From the result it can be found that complexes

maintain higher activity from 60°C to 90°C, which gives many advantages in industrial practices. A remarkable event is that the activity of complex 4 increases rapidly when the temperature increases from 30°C to 60°C and then raise very slowly as temperature increases from 60°C to 90°C, which differ from that of similar symmetric complex.³⁰ It is also found that under high temperature 90°C, the activity of titanium complexes decreases in the order: 1 (t -Bu, H) > 5 (Me_3Si , H) > 3 (t -Bu, allyl) > 2 (t -Bu, Me). The other notable phenomenon is that the catalytic activity of titanium complex 1 is higher than that of zirconium complex 4 having the same Ligand at 90°C, which implies the stability of titanium complexes is higher than that of zirconium at high temperature. The effect of temperature on molecular weight was shown in Table 1.

From Table 1, it was found the molecular weight obtained with titanium complexes decreases slowly as the reaction temperature raises, which implies that the rate of polymer chain transfer is promoted with temperature.

The influence of time on catalytic activity was shown in Figure 5. It is obvious that all the titanium complexes activity slowly decreases with the time. This phenomenon may be because of

Table 1. The Effect of Temperature on Molecular Weight

Complex	$M_n (\times 10^5 \text{g/mol})$				
	30°C	45°C	60°C	75°C	90°C
1(t -Bu,H,Ti)	*	/	6.54	/	3.27
2(t -Bu,Me,Ti)	*	8.35	7.01	5.31	2.46
3(t -Bu,allyl,Ti)	6.37	4.18	3.02	2.87	2.68
4(t -Bu,H,Zr)	4.58	5.26	5.64	4.82	4.71
5(Me_3Si ,H,Ti)	*	8.31	3.01	5.37	2.67

The sample cannot dissolve in decahydronaphthalene at 135°C. [Cat.] = 2.0 μmol ; Al/M = 1000:1; t = 30 min; Total volume = 25 mL; P_{ethylene} = 1.0 MPa.

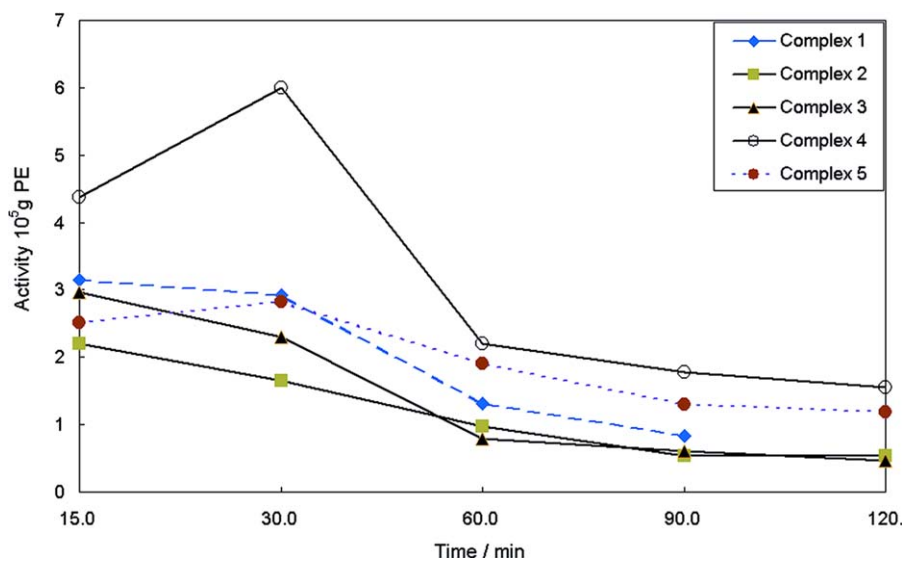


Figure 5. Influence of time on catalytic activity. Condition: [Cat.] = 2.0 μmol , Al/M = 1000:1, $T = 60^\circ\text{C}$, Total volume = 25 mL, $P_{\text{ethylene}} = 1.0$ MPa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the deactivation of catalyst with the time prolongation. From the result it can also be found that there is appropriate time point, lower than or higher than the point will lead up to lower activity. It is noteworthy that the catalytic activity of complex 4 increases with time and then descends rapidly when the time over 30 min, which implies the zirconium complex spend some time to get activated state and deactivate rapidly as time extending.

The influence of time on molecular weight of polymer was summarized in Figure 6.

The results of Figure 6 imply that the reaction time has little effect on molecular weight gain with complexes 1 and 2. It is a interesting finding from the result, it implies that the mechanism of polymerization catalyzed with complexes 1 and 2 is not similar to that

of the other complexes; it is well known that the polymer molecular weight is determined by the ratio of chain propagation to chain transfer. We think the time to reach equilibrium of chain propagation and chain termination catalyzed with complexes 1 and 2 is less than 30 min, which means prolongation of the time of the polymerization reaction has few influence on the molecular weight of the mPE obtained. On the other way, for complexes 3, 4, and 5, the polymer molecular weight increases slowly as time is extending, which suggests that the process of chain propagation maintains more time and the polymer molecular weight increase slowly with time prolongation.

Copolymerization of Ethylene with 1-Hexene

These complexes show the notable characteristics in ethylene polymerization; we are thus encouraged to investigate their

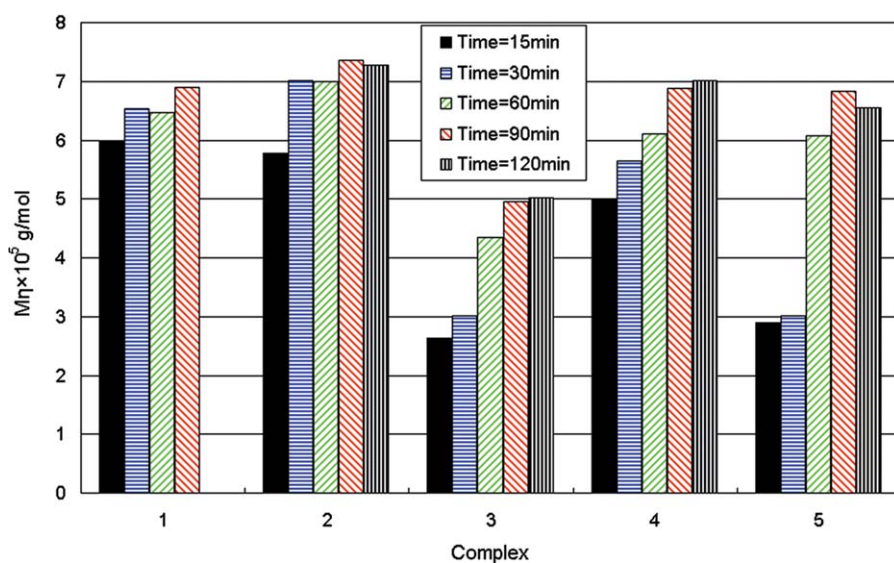


Figure 6. Influence of time on molecular weight of polymer. Condition: [Cat.] = 2.0 μmol , Al/M = 1000:1, $T = 60^\circ\text{C}$, Total volume = 25 mL, $P_{\text{ethylene}} = 1.0$ MPa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 2. Result of Random Copolymerization of Ethylene with 1-Hexene with Complexes 1–5

Complex	1-Hexene (mL)	Act.	M_n	M_n (g/mol)	M_w (g/mol)	MWD ^a
1	1	3.558	5.62			
	2	2.989	5.16	7409	80,183	10.82
	3	1.290				
	4	0.373				
2	1	1.611	2.23			
	2	1.587	2.01	4873	77,079	15.82
3	1	0.983	1.16			
	2	0.401	1.09	2593	31,087	11.99
4	1	8.024	0.55			
	2	10.696	0.43	31,571	104,454	3.31
5	1	2.862	4.65			
	2	3.355	4.22	3047	52,591	17.26

^aCondition: [Cat.] = 2.0 μ mol, Al/M = 1000:1, t = 30 min, T = 60°C, Total volume = 25 mL, P_{ethylene} = 1.0 MPa; Act., $\times 10^5$ g/(mol·M·h); M_n , $\times 10^5$ g/mol. M_n , M_w , and PD calculated from GPC. H% calculated from ^{13}C NMR.

copolymerization behavior. Table 2 summarizes the results for ethylene/1-hexene copolymerization by the complexes /MAO catalytic systems.

From the results of ethylene/1-hexene copolymerization, we found that the molecular weight for the copolymer prepared by complexes 1–5 was lower than those of polyethylene. It is noteworthy that complex 4 exhibits the highest catalytic activity (1.07×10^6 g/mol Zr·h) among the catalytic systems. It is also noted that the catalytic activity increases in the order 3 (*t*-Bu, allyl: 0.983×10^5 g/mol Ti·h) < 2 (*t*-Bu, methyl: 1.611×10^5 g/mol·Ti·h) < 5 (Me_3Si , H: 2.862×10^5 g/mol Ti·h) < 1 (*t*-Bu, H: 3.558×10^5 g/mol·Ti·h) < 4 (*t*-Bu, H: 1.07×10^6 g/mol Zr·h) under the same polymerization conditions (1-hexene = 2.0 mL), the order is similar to that of ethylene polymerization result, which indicates that the steric bulkiness effect also plays important role in copolymerization. The PD of 4 is lowest in complexes 1–5 just like that of ethylene polymerization, so we suggest that the same Ligand has less effect on zirconium complex than that of titanium complex. In addition the effect of the amount of 1-hexene on catalytic activity was also investigated. For complexes 4 and 5, the activity increases as the 1-hexene

content in reactor augments from 1.0 to 2.0 mL, we attribute it to comonomer effect according to Zakharov⁴⁰ theory. On the contrary, the activity of complexes 1–3 decreased as 1-hexene content augment.

The copolymer microstructures are analyzed on the basis of ^{13}C NMR with reference to Randall's^{41,42} report. Results of the analysis are given in Table 3. From the ^{13}C NMR spectrum of copolymer, only *n*-butyl branch has been found. From Table 3, it is found that in every case, the content of the ethylene unit is higher than that of the 1-hexene unit and no HH component was found, which means the 1-hexene unit is isolated in the copolymer chain because of the low incorporation. Taking into account the above results, the effect of substituent in bridge fragment plays an essential role in both the catalytic activity and the monomer sequence distributions in ethylene/1-hexene copolymerization.

From the result, it is found that complex 3 shows the highest 1-hexene incorporation ability (1.57% mol) and there are no [HH] fragments in copolymer chain, which implies that the 1-hexene exist random in polymer.

Table 3. Dyad and Triad Distribution of Poly(ethylene-*co*-1-hexene)s with Complexes 1–5/MAO

Sample	HH (%mol)	HE (%mol)	EE (%mol)	HHH (%mol)	HHE (%mol)	EHE (%mol)	HEH (%mol)	EEH (%mol)	EEE (%mol)	H % (%mol)
1	0	5.19	94.81	0	0	4.17	0	2.05	93.78	1.42
2	0	2.29	97.71	0	0	2.10	0	0.39	97.57	1.08
3	0	2.28	97.72	0	0	2.13	0	0.30	97.54	1.57
4	0	4.27	95.73	0	0	3.68	0	1.18	95.14	1.08
5	0	1.74	98.26	0	0	1.43	0	0.61	97.96	0.58

^aCalculated from ^{13}C NMR spectra. EE = EEE + 1/2EEH,

EH = 1/2EHH + 1/2HEE + EHE + HEH, HH = HHH + 1/2HHE. H, 1-hexene; E, ethylene. 1-Hexene content in copolymer determined by ^{13}C NMR spectra.

CONCLUSION

We synthesized a series of new asymmetric double Me₂Si-bridged binuclear metallocene complexes and examined their catalytic behaviors for ethylene polymerization and copolymerization with 1-hexene in the presence of MAO. As a result of polymerizations, it was found that the substituents on the bridged Cp ring play an important role in the catalytic performance of this series of complexes. Among them, 4/MAO system exhibits the highest catalytic activity for the polymerization of ethylene and complex 3 shows the highest 1-hexene incorporation ability (1.57% mol).

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