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A biphenylene-bridged dinuclear constrained geometry titanium complex for ethylene and ethylene/1-octene polymerizations

Min Hyung Lee [a,*], Myung Hwan Park [b], Woo Young Sung [a], Seong Kyun Kim [b], AuJiRu Son [c], Youngkyu Do [b,**]

[a] Department of Chemistry and Energy Harvest-Storage Research Center, University of Ulsan, Ulsan 680–749, Republic of Korea
[b] Department of Chemistry, KAIST, Daejeon 305–701, Republic of Korea
[c] Catalyst Synthetic Laboratory, Kumho Polychem, Yeosu 555-290, Republic of Korea

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ABSTRACT

Permethylated cyclopentadienyl dinuclear constrained geometry titanium catalyst, $[\mu\text{-}(C_6H_4)_2\text{-}2,2']\{(\eta^5\text{-}C_5Me_3)[1\text{-}Me_2Si(\eta^1\text{-}N\text{-}{}^tBu)](TiCl_2)\}_2$ (**BPTi₂**) linked by a biphenylene bridge was synthesized and tested in ethylene and ethylene/1-octene polymerizations upon activation by TIBA (triisobutylaluminum)/$[Ph_3C][B(C_6F_5)_4]$. When compared with the corresponding highly active, mononuclear analogs, $Me_2Si(\eta^5\text{-}2\text{-}PhC_5Me_3)(\eta^1\text{-}N\text{-}{}^tBu)TiCl_2$ (**PhTi₁**) and $Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^1\text{-}N\text{-}{}^tBu)TiCl_2$ (**MeTi₁**), **BPTi₂** exhibits significantly increased molecular weight of polymer (>two-fold), as well as high level of activity and 1-octene incorporations in ethylene and ethylene/1-octene polymerizations. Although the lower activity was observed at high 1-octene feeds, the combined effects of rigidity and electronic conjugation induced by the biphenylene bridge might be responsible for the observed polymerization properties of **BPTi₂**.

1. Introduction

One of the major advances in single-site olefin catalyst systems is the development of constrained geometry catalysts (CGCs) based on the linked cyclopentadienyl-amido ancillary ligand, capable of inducing efficiently the copolymerization of ethylene with higher α-olefins to form linear low-density polyethylene (LLDPE) [1–12]. In addition to high activity and high molecular weight of polymer, most marked in CGCs are the catalytic properties involving comonomer incorporation and distribution and the formation of long-chain branching (LCB) [13–17]. In this regard, recent studies on the dinuclear indenyl-CGCs connected by flexible bridging groups provided new impetus to the improvement of catalytic performance of existing mononuclear CGCs [18–32]. The intriguing catalytic properties such as higher α-olefin incorporation [30], high activity in styrene polymerization [26], and branched or significantly increased molecular weights in ethylene polymerization [24,25,31] were reported mainly due to the cooperative interactions between two active centers. Despite their unique properties, however, the evaluation of catalytic properties of dinuclear systems has not been clearly described in terms of comparative studies with the highly active, prototypical cyclopentadienyl-CGCs, such as $Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^1\text{-}N\text{-}{}^tBu)TiCl_2$ (**MeTi₁**) for a commercial goal (Chart 1). Moreover, it is necessary for dinuclear CGCs to attain high activity, high molecular weight, and effective comonomer enchainment, especially for the utilization in a high-temperature solution process [15,16,33]. Regarding dinuclear cyclopentadienyl-CGCs, Lee and coworkers have reported an example of the highly active CGC linked through an *o*-phenylene *ansa*-bridge [34].

In an effort to develop dinuclear catalytic systems, we disclosed that the dinuclear group 4 metal complexes linked by a rigid and/or a modulated biphenylene bridge between two cyclopentadienyl rings can exhibit the enhanced polymerization properties such as increase of molecular weight and catalytic activity in ethylene and

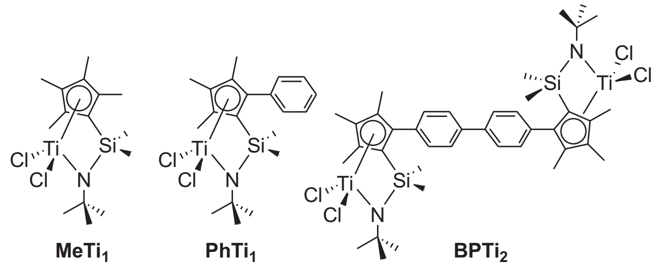

Chart 1.

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* Corresponding author. Tel.: +82 52 259 2335; fax: +82 52 259 2348.

** Corresponding author. Tel.: +82 42 350 2829; fax: +82 42 350 2810.
E-mail addresses: lmh74@ulsan.ac.kr (M.H. Lee), ykdo@kaist.ac.kr (Y. Do).

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styrene polymerizations [35,36]. These results prompted us to apply the biphenylene bridge to the synthesis of novel dinuclear CGC possessing two sterically isolated ansa-units. It is anticipated that the structure could be beneficial to both the stabilization of cationic active centers by electronic conjugation effect and the prevention of mutual steric hindrance that may occur between metal centers located in proximity. Herein we report the synthesis of a dumbbell-like, permethylated cyclopentadienyl dinuclear Ti-CGC (**BPTi$_2$**) and the polymerization behaviors in ethylene and ethylene/1-octene polymerizations in comparison with the corresponding highly active, mononuclear Ti-CGC analogs.

2. Experimental

2.1. General considerations

All operations were performed under an inert nitrogen atmosphere using standard Schlenk and glove box techniques. Anhydrous grade solvents (Aldrich) were purified by passing through an activated alumina column. All solvents were stored over activated molecular sieves (5Å). Chemicals were used without any further purification after purchasing from Aldrich (4,4′-Dibromobiphenyl, *n*-BuLi (2.5 M solution in *n*-hexane), Me_2SiCl_2, *tert*-Butylamine, PhMgBr (3.0 M solution in Et_2O), *para*-Toluenesulfonic acid monohydrate (*p*-TsOH•H_2O)), and Strem ($TiCl_3(thf)_3$, AgCl, $Li(C_5Me_4H)$). 2,3,4-Trimethylcyclopent-2-enone [37], $Me_2Si(\eta^5\text{-}2\text{-}PhC_5Me_3)(\eta^1\text{-}N\text{-}{}^tBu)TiCl_2$ (**PhTi$_1$**) [38], and $Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^1\text{-}N\text{-}{}^tBu)TiCl_2$ (**MeTi$_1$**) [11,12,39] were prepared analogously according to the literature procedures. Polymerization-grade ethylene monomer from Honam Petrochemical Co. was used after purification by passing through Labclear™ and Oxiclear™ filters. 1-Octene (Aldrich) was purified by passing through an activated alumina column. Triisobutylaluminum (TIBA, 1.0 M solution in toluene, Aldrich) and $[Ph_3C][B(C_6F_5)_4]$ (Asahi Glass Co.) were used as received. $CDCl_3$ was dried over activated molecular sieves (5Å), and used after vacuum transfer to a Schlenk tube equipped with a J. Young valve. ^1H and ^{13}C NMR spectra of compounds were recorded on a Bruker Avance 400 spectrometer at ambient temperature. All chemical shifts are reported in δ units with reference to the residual peaks of $CDCl_3$ for proton (7.24 ppm) and carbon (77.0 ppm) chemical shifts. Elemental analyses (FISONS EA 1110) and HR EIMS measurement (FISONS VG Auto Spec) were carried out at KAIST.

2.2. Synthesis of catalyst

2.2.1. Synthesis of 4,4′-$(C_5Me_3H_2)_2(C_6H_4)_2$ *(1)*

A slurry of 9.36 g (30.0 mmol) of 4,4′-dibromobiphenyl in 40 mL of diethyl ether was treated with two equiv of *n*-BuLi (24.0 mL) at −30 °C. Upon warming, the reaction mixture became a clean solution, and was allowed to warm to 0 °C. A slow formation of a white precipitate was observed, and further stirred for an additional 0.5 h at this temperature. The reaction mixture was finally allowed to warm to room temperature and stirred for another 2 h. A colorless solution over the precipitate was then decanted off, and 30 mL of THF was added to the resulting dilithium salt. The mixture was cooled to −78 °C, and subsequently two equiv of 2,3,4-trimethylcyclopent-2-enone (7.46 g) in 20 mL of THF was slowly added via cannula at −78 °C. The reaction mixture was slowly allowed to warm to room temperature and stirred overnight. The resulting light orange solution was treated with 30 mL of saturated aqueous solution of NH_4Cl to stop the reaction. Next, the organic portion was separated and the aqueous layer was further extracted with diethyl ether (50 mL). The combined organic portions were dried over $MgSO_4$, filtered, and evaporated to dryness, affording a colorless oily product. The crude product was redissolved in CH_2Cl_2 (30 mL), and a catalytic amount of *p*-TsOH (ca. 0.1 g) was added as solid into the solution at room temperature. An ivory solid was immediately formed, and the stirring was further continued for about 0.5 h. The volume of the resulting reaction mixture was reduced to wet, and 30 mL of *n*-hexane was poured in to the flask in order to precipitate the product and dissolve out unreacted materials. The large amount of an ivory solid obtained was filtered on a glass frit and successively washed with ethanol (30 mL), diethyl ether (30 mL), and *n*-pentane (30 mL). Drying *in vacuo* afforded 7.13 g of **1** (Yield: 65%). ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 7.58$ (d, 4H, C_6H_4), 7.40 (d, 4H, C_6H_4), 3.22 (s, 4H, $C_5Me_3H_2$), 2.11 (s, 6H, $C_5Me_3H_2$), 2.00 (s, 6H, $C_5Me_3H_2$), 1.87 (s, 6H, $C_5Me_3H_2$). ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 139.43$, 137.76, 137.51, 136.87, 135.40, 135.36, 127.75, 126.62, 46.74 (C_5Me_3), 13.61 (C_5Me_3), 13.29 (C_5Me_3), 11.24 (C_5Me_3). Anal. Calcd for $C_{28}H_{30}$: C, 91.75; H, 8.25. Found: C, 92.18; H, 8.38.

2.2.2. Synthesis of $[2,2'\text{-}(C_6H_4)_2][1\text{-}Me_2Si(NH\text{-}{}^tBu)(C_5Me_3H)]_2$ *(2)*

A slurry of 1.83 g (5.0 mmol) of **1** in 30 mL of THF was treated with two equiv of *n*-BuLi (4.0 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. To the resulting yellow slurry was added an excess amount of Me_2SiCl_2 (1.5 × 2 equiv, 1.82 mL) at −78 °C. The reaction mixture was slowly allowed to warm to room temperature and stirred overnight. The colorless solution was evaporated to dryness, and then extracted with 30 mL of CH_2Cl_2. Filtration followed by removal of the solvent *in vacuo* afforded an ivory solid of $[2,2'\text{-}(C_6H_4)_2][1\text{-}Me_2SiCl(C_5Me_3H)]_2$ in quantitative yield. ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 7.62$ (d, 4H, C_6H_4), 7.29 (d, 4H, C_6H_4), 3.81 (s, 2H, C_5Me_3H), 2.15 (s, 6H, C_5Me_3H), 2.08 (s, 6H, C_5Me_3H), 1.93 (s, 6H, C_5Me_3H), −0.05 (s, 12H, Me_2Si). ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 139.88$, 138.06, 137.96, 136.64, 136.36, 134.71, 129.36, 126.45, 54.87 (SiC_5Me_3), 14.74 (C_5Me_3), 12.86 (C_5Me_3), 11.22 (C_5Me_3), 2.94 (Me_2Si), −2.39 (Me_2Si).

The obtained $[2,2'\text{-}(C_6H_4)_2][1\text{-}Me_2SiCl(C_5Me_3H)]_2$ was dissolved in 30 mL of THF, and cooled to −78 °C. Next, the solution was treated with a three-fold excess amount of $^tBuNH_2$ (3 × 2 equiv, 3.15 mL). Upon warming, colorless salts were gradually formed. The reaction mixture was stirred overnight and then evaporated to dryness. Extraction with 30 mL of Et_2O and filtration followed by removal of the solvent *in vacuo* afforded light yellow sticky foam of **2** in 96% yield. ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 7.59$ (d, 4H, C_6H_4), 7.28 (d, 4H, C_6H_4), 3.59 (s, 2H, C_5Me_3H), 2.08 (s, 6H, C_5Me_3H), 2.05 (s, 6H, C_5Me_3H), 1.90 (s, 6H, C_5Me_3H), 0.94 (s, 18H, $NHCMe_3$), 0.32 (s, 2H, $NHCMe_3$), −0.13 (s, 6H, Me_2Si), −0.30 (s, 6H, Me_2Si). ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 138.02$, 137.94, 137.61, 137.14, 136.81, 136.02, 129.55, 126.42, 55.52 ($NCMe_3$), 49.24 (SiC_5Me_3), 33.49 ($NCMe_3$), 15.06 (C_5Me_3), 12.66 (C_5Me_3), 11.18 (C_5Me_3), 0.29 (Me_2Si). HR EIMS: *m/z* calcd for $C_{40}H_{60}N_2Si_2$, 624.4295; found, 624.4272.

2.2.3. Synthesis of $[\mu\text{-}(C_6H_4)_2\text{-}2,2']\{(\eta^5\text{-}C_5Me_3)[1\text{-}Me_2Si(\eta^1\text{-}N\text{-}{}^tBu)](TiCl_2)\}_2$ *(**BPTi$_2$**)*

A solution of 2.50 g of $[2,2'\text{-}(C_6H_4)_2][1\text{-}Me_2Si(NH\text{-}{}^tBu)(C_5Me_3H)]_2$ (4.0 mmol) in 40 mL of THF was treated with four equiv of *n*-BuLi (6.4 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 2 h. The resulting dark brownish-green solution was then added via cannula to the pre-cooled flask containing THF (40 mL) slurry of $TiCl_3(THF)_3$ (2.96 g, 8.0 mmol) at −78 °C with vigorous stirring. The reaction mixture was slowly allowed to warm to room temperature and stirred overnight. To the resulting dark green solution was transferred 2.2 equiv of AgCl (1.26 g) as solid. An immediate color change to dark orange-brown with the gradual precipitation of Ag^0 was observed. After stirring for 1 h, the reaction mixture was evaporated to dryness. The resulting dark sticky residue was redissolved in 50 mL of a mixed solvent of *n*-hexane/CH_2Cl_2 ($v/v = 2:1$), and filtered. Removal of the solvent followed by thorough washing with *n*-hexane several times resulted in a bright brown powder. Drying *in vacuo* afforded 2.43 g of **$BPTi_2$** in 71% yield. ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 7.60$ (br d, 8H, C_6H_4), 2.29 (s, 6H, C_5Me_3H), 2.24 (s, 6H, C_5Me_3H), 2.17 (s, 6H, C_5Me_3H), 1.38 (s, 18H, $NHCMe_3$), 0.65 (s, 6H, Me_2Si), −0.12 (s, 6H, Me_2Si). ^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 147.30$, 142.56, 139.83, 137.76, 137.21, 134.69, 126.14 (2C), 104.37 (SiC_5Me_3), 63.16 ($NCMe_3$), 32.59 ($NCMe_3$), 16.79 (C_5Me_3), 13.38 (C_5Me_3), 13.31 (C_5Me_3), 4.92 (Me_2Si), 4.26 (Me_2Si). Anal. Calcd for $C_{40}H_{56}Cl_4N_2Si_2Ti_2$: C, 55.95; H, 6.57; N, 3.26. Found: C, 55.28; H, 6.96; N, 3.04.

2.3. Polymerization procedure

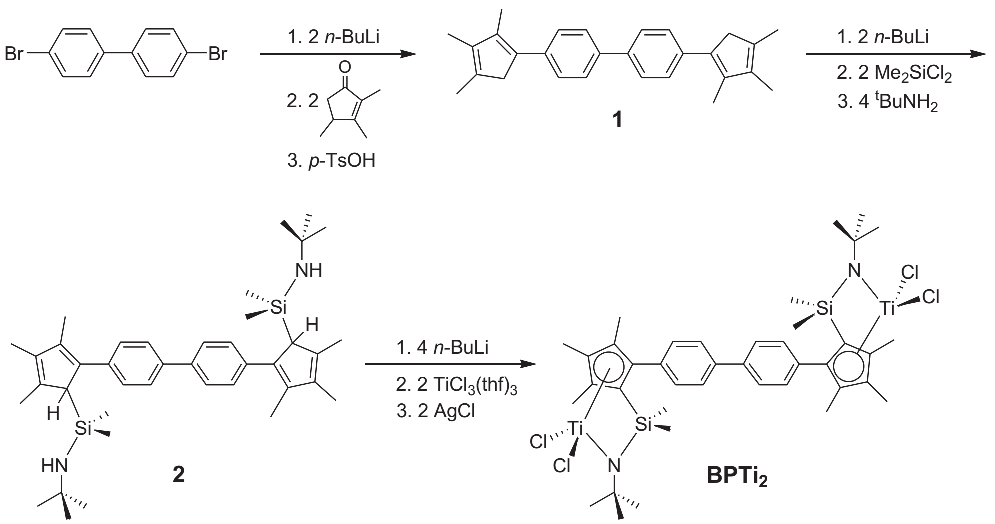
Into a well-degassed 250 mL-glass reactor equipped with a 3 cm-egg shaped magnetic bar, freshly dried toluene (98.0 mL) was transferred, and the reactor was adjusted to the desired reaction temperature using an external bath. Ethylene monomer was then saturated at 1 bar with vigorous stirring for at least 10 min after degassing with it several times. In the case of copolymerization, 1-octene was charged via a syringe at the initial stage of ethylene saturation and the saturation was further continued for 10 min. During the period of ethylene saturation, catalyst activation was separately carried out; a toluene solution of catalyst (0.01 M of [Ti]) was first treated with 50 equiv of TIBA, which was allowed to react for 10 min, providing 6.67 mM of in situ alkylated Ti solution. The measured volume of this solution which fixes the final concentration of an activated catalyst solution at 2.00 mM based on [Ti] was then added to a toluene solution, typically 3.00 mM concentration, of 1.1 equiv of $[Ph_3C][B(C_6F_5)_4]$. The slightly excess amount of $[Ph_3C][B(C_6F_5)_4]$ was employed in order to ensure complete catalyst activation. Next, the activated catalyst solution (4.0 μmol of Ti, 2.0 mL) was quickly injected into the reactor. As soon as catalyst injection, rapid increase of viscosity in the reaction medium was observed, particularly in ethylene homopolymerization by **$BPTi_2$**. All the reactions were quenched after 1 min by the injection of ca. 1 mL of 10% HCl solution of EtOH. The resultant mixture was then poured into the large volume of EtOH (500 mL) and stirred for 1 h. The precipitated polymer was subsequently collected by filtration, and washed with EtOH several times (ca. 200 mL). The resulting polymers were finally dried in a vacuum oven at 70 °C to constant weight. In the case of sticky polymers, usually copolymers of high 1-octene content, the sticky residue formed after the addition of EtOH was obtained by decanting the solution followed by washing with EtOH. The waxy poly(1-octene)s were acquired differently as described above; After quenching by ca. 1 mL of 10% HCl solution of EtOH, the bulk polymerization mixture was evaporated to dryness under vacuum. The residue was then extracted with $CHCl_3$ and washed with aqueous solution of 10% HCl to remove any insoluble materials. The organic phase was separated, evaporated, and finally dried in a vacuum oven at 70 °C.

2.4. Polymer characterization

^{13}C NMR spectra of the polymers were recorded on either a Bruker Avance 400 (^{13}C; 100.62 MHz) or a Bruker AMAX 500 (^{13}C; 125.77 MHz) spectrometer at 120 °C with 90° pulse angle, 2 s acquisition time, and 8 s relaxation delay. The samples were dissolved in 1,1,2,2,-tetrachloroethane-d_2 to form a 10 wt.-% solution (ca. 90 mg/0.5 mL) in 5-mm tubes. All the measurements were performed after complete dissolution by pre-heating the samples to about 110 °C in an oil bath. The chemical shift value of main backbone methylene ($\delta^+\delta^+ = 29.98$ ppm) was used as an internal standard. Peak assignments and the estimation of 1-octene content in the polymers were made according to the reported literatures [40,41]. The molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the polymers were analyzed by high-temperature gel-permeation chromatography (GPC) using a Polymer Laboratories PL 220 at 140 °C in 1,2,4-trichlorobenzene with a flow rate of 1.00 mL/min. The molecular weight (M_w) measured was calibrated using narrow polystyrene standards as a reference. The melting transition (T_m) of the polymers from **$BPTi_2$** was measured by differential scanning calorimetry (DSC, TA Instrument Q100) at a heating rate of 10 °C/min. Any thermal history in the polymers was eliminated by the first heating the samples to 180 °C at 20 °C/min, cooling to −80 °C at 20 °C/min, and then recording the second DSC scan from −80 °C to 180 °C.

3. Results and discussion

A new biscyclopentadienyl ligand, 4,4′-$(C_5Me_3H_2)_2(C_6H_4)_2$ (**1**) was designed to achieve the biphenylene-bridged permethylated dinuclear CGC (**$BPTi_2$**) in which the biphenylene group is linked to an α-position to the bridgehead carbon atom of the Cp ring to maintain a sterically open nature. **1** was prepared from the reaction of dilithium salt of 4,4′-dibrombiphenyl and two equiv of 2,3,4-trimethylcyclopent-2-enone followed by dehydration (Scheme 1).



Scheme 1. Synthesis of a biphenylene-bridged dinuclear Ti-CGC (**$BPTi_2$**).

Table 1
Ethylene and ethylene/1-octene polymerization results with **BPTi$_2$**, **PhTi$_1$**, **MeTi$_1$**/Al(^{i}Bu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] catalytic systems[a].

Run	Catalyst	Amt of cat. (μmol)	1-Octene feed (mL)	T_p (°C)	Yield (g)	Activity[c]	10^{-3} M_w[d] (g mol^{-1})	M_w/M_n[d]	1-Octene content[e] (mol%)	T_m[f] (°C)
1	**BPTi$_2$**	2.0	0	25	0.48	7.20×10^6	1329	2.61		134.6
2	**BPTi$_2$**	2.0	0	50	0.64	9.60×10^6	661	2.38		134.5
3	**BPTi$_2$**	2.0	0	75	0.68	1.02×10^7	348	2.84		133.8
4	**PhTi$_1$**	4.0	0	25	0.73	1.10×10^7	450	2.36		–[g]
5	**PhTi$_1$**	4.0	0	50	0.60	9.00×10^6	305	2.36		–
6	**PhTi$_1$**	4.0	0	75	0.56	8.40×10^6	211	3.01		–
7	**MeTi$_1$**	4.0	0	50	0.57	8.55×10^6	266	3.19		–
8	**BPTi$_2$**	2.0	0.5	50	0.97	1.46×10^7	322	2.65	6.3	87.8
9	**BPTi$_2$**	2.0	1.0	50	1.15	1.73×10^7	243	2.59	12.1	59.4
10	**BPTi$_2$**	2.0	2.0	50	1.27	1.91×10^7	227	2.19	21.5	n/o[h]
11	**BPTi$_2$**	2.0	5.0	50	1.46	2.19×10^7	137	2.12	43.7	n/o
12[b]	**BPTi$_2$**	2.0	30.0	50	0.12	1.80×10^6	15	1.34		
13	**PhTi$_1$**	4.0	0.5	50	1.06	1.59×10^7	132	3.21	6.3	–
14	**PhTi$_1$**	4.0	1.0	50	1.30	1.95×10^7	90	3.10	11.3	–
15	**PhTi$_1$**	4.0	2.0	50	1.82	2.73×10^7	54	2.65	20.6	–
16	**PhTi$_1$**	4.0	5.0	50	2.59	3.89×10^7	43	2.24	43.1	–
17[b]	**PhTi$_1$**	4.0	30.0	50	0.15	2.25×10^6	17	1.42		–
18	**MeTi$_1$**	4.0	1.0	50	1.26	1.89×10^7	138	3.04	11.3	–

[a] Polymerization conditions: $P_E = 1$ bar; [Al]/[Ti] = 50; [B]/[Ti] = 1.1; solvent = 100 mL of toluene; $t_p = 1.0$ min.
[b] Bulk polymerization of 1-octene.
[c] Activity given in units of g polymer (mol Ti h bar)$^{-1}$.
[d] Determined by GPC.
[e] Determined by ^{13}C NMR.
[f] Determined by DSC.
[g] Not determined.
[h] Not observed.

This synthetic route is quite straightforward and the crystalline **1** was obtained in good yield freed from any mono-substituted side products. Despite poor solubility in common organic solvents such as THF, ether, and CH$_2$Cl$_2$, **1** can be readily converted into the corresponding dilithium salt in THF, which subsequently reacted with two equiv Me$_2$SiCl$_2$ and then excess ^{t}BuNH$_2$ to afford the final CGC ligand (**2**) as sticky foam in high yield (96%). Synthesis of the dinuclear **BPTi$_2$** was directed by a usual method applied to the synthesis of mononuclear CGCs using tetralithium salt of **2** and two equiv of TiCl$_3$(thf)$_3$ in THF. The formation of **BPTi$_2$** was confirmed by the ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. However, attempts to obtain single crystals of **BPTi$_2$** have failed due to poor crystallinity. Along with **BPTi$_2$**, the corresponding mono-CGCs, **PhTi$_1$** and **MeTi$_1$** were prepared analogously for a comparison study.

To investigate the catalytic properties of **BPTi$_2$** in olefin polymerization, ethylene polymerization behavior was first examined. In situ alkylation using triisobutylaluminum (TIBA) followed by borate ([Ph$_3$C][B(C$_6$F$_5$)$_4$]) activation of **BPTi$_2$** afforded a highly active catalytic system in ethylene polymerization (Table 1).

According to the comparative result with the **PhTi$_1$** system, the overall activity of **BPTi$_2$** is almost in a similar range, but the retention of high activity at elevated temperatures is particularly observed. In contrast, the activity of **PhTi$_1$** decreases with increasing temperature as reported [42], implying an enhanced thermal stability of **BPTi$_2$**. Moreover, the activity of **BPTi$_2$** is even larger than that of **MeTi$_1$** under the identical conditions. It is interesting to note that the molecular weight of polyethylenes by **BPTi$_2$** is nearly 2–3 times greater than those by **PhTi$_1$** and **MeTi$_1$** in a whole reaction temperature range. From the fact that **PhTi$_1$** produces polyethylenes having slightly increased molecular weight than **MeTi$_1$** at 50 °C (run 5 vs. run 7), the much increased molecular weight by **BPTi$_2$** is quite remarkable (Fig. 1). The narrow molecular weight distribution (M_w/M_n) from **BPTi$_2$**, as similar to that of polyethylenes obtained with the mononuclear CGCs, also indicates that the two titanium active centers behave as single active sites.

Based on the foregoing ethylene polymerization results, the detailed ethylene/1-octene copolymerization was performed, especially at 50 °C where **BPTi$_2$** and **PhTi$_1$** exhibited nearly same

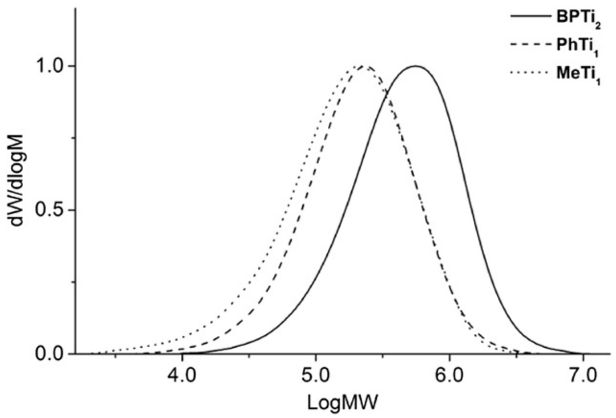


Fig. 1. GPC curves of polyethylenes from **BPTi$_2$**, **PhTi$_1$**, and **MeTi$_1$** at 50 °C (runs 2, 5, and 7, respectively in Table 1).

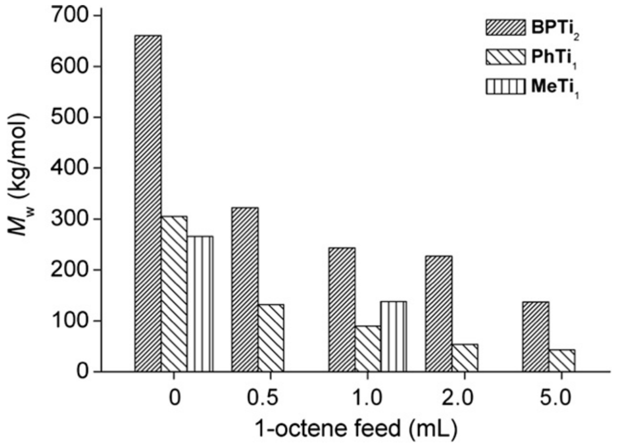


Fig. 2. Comparison of molecular weight (M_w) of polyethylenes and poly(ethylene-*co*-1-octene)s from **BPTi$_2$**, **PhTi$_1$**, and **MeTi$_1$** at 50 °C.

activity in ethylene polymerization (Table 1). The polymerization results upon variation of 1-octene amount in the feed indicate that **BPTi$_2$** acts as a highly active catalyst in ethylene/1-octene copolymerization. The activity of both **BPTi$_2$** and **PhTi** systems is higher than that in the corresponding ethylene homopolymerization, and that the higher the 1-octene feed, the higher activity results in [43,44]. However, the lower activity of **BPTi$_2$** than **PhTi$_1$** is observed at the increased 1-octene feeds (2.0 and 5.0 mL), while the activity is in a similar range at the moderate 1-octene feeds (0.5 and 1.0 mL). On the other hand, the molecular weight of copolymers by **BPTi$_2$**, which is lower than those of polyethylenes and is decreasing with increasing 1-octene feed, is 2–4 times greater than those by **PhTi$_1$** and **MeTi$_1$** whose values show a slight difference (Fig. 2). Although the moderate increase in the molecular weight of poly(ethylene-*co*-1-hexene) has recently been observed for the cyclopentadienyl dinuclear Ti-CGCs [34], the consistently observed large increase of molecular weight by **BPTi$_2$** in both polyethylene and poly(ethylene-*co*-1-octene) over various reaction conditions could be an interesting polymerization feature of the present dinuclear Ti-CGC system.

Regarding molecular weight of polymer, it was reported that similar values are typically observed between mono and dinuclear indenyl Ti-CGCs linked by flexible bridges [30], while significantly high molecular weight polyethylene from dinuclear Zr-CGCs can be achievable via a macromolecular reinsertion process [24,25]. Since the molecular weight of polymer is much governed by electronic effect of ligand [17,33], the increase of molecular weight by **BPTi$_2$** appears to be mainly attributed to the electronic effect of the biphenylene bridge on both cationic active centers. Exclusion of mutual steric effect between the active centers caused by the rigid and isolated ansa-nature in **BPTi$_2$** may be supportive of the large involvement of electronic effect on molecular weight (*vide infra*). The similar increase of molecular weight of polyethylene, even though a less extent to the given system, was previously observed for the dinuclear zirconocenes linked by a biphenylene bridge [35,36].

^{13}C NMR analyses of copolymers reveal high 1-octene incorporation in the copolymers obtained from **BPTi$_2$** as comparable to those from **PhTi$_1$** and **MeTi$_1$** under identical 1-octene feeds. The estimation of the comonomer contents at the different comonomer feeds indicates that the incorporation of 1-octene into the polyethylene backbone gradually increases with increasing comonomer concentration in the feed. Furthermore the ^{13}C NMR spectra, for example, obtained at 1-octene feed of 1.0 mL, exhibit almost similar carbon peak positions and intensities for all three systems (Fig. 3). In conjunction with the narrow M_w/M_n of all the copolymers from **BPTi$_2$**, these results indicate that (co)monomer insertions occur independently at each isolated metal unit of **BPTi$_2$**.

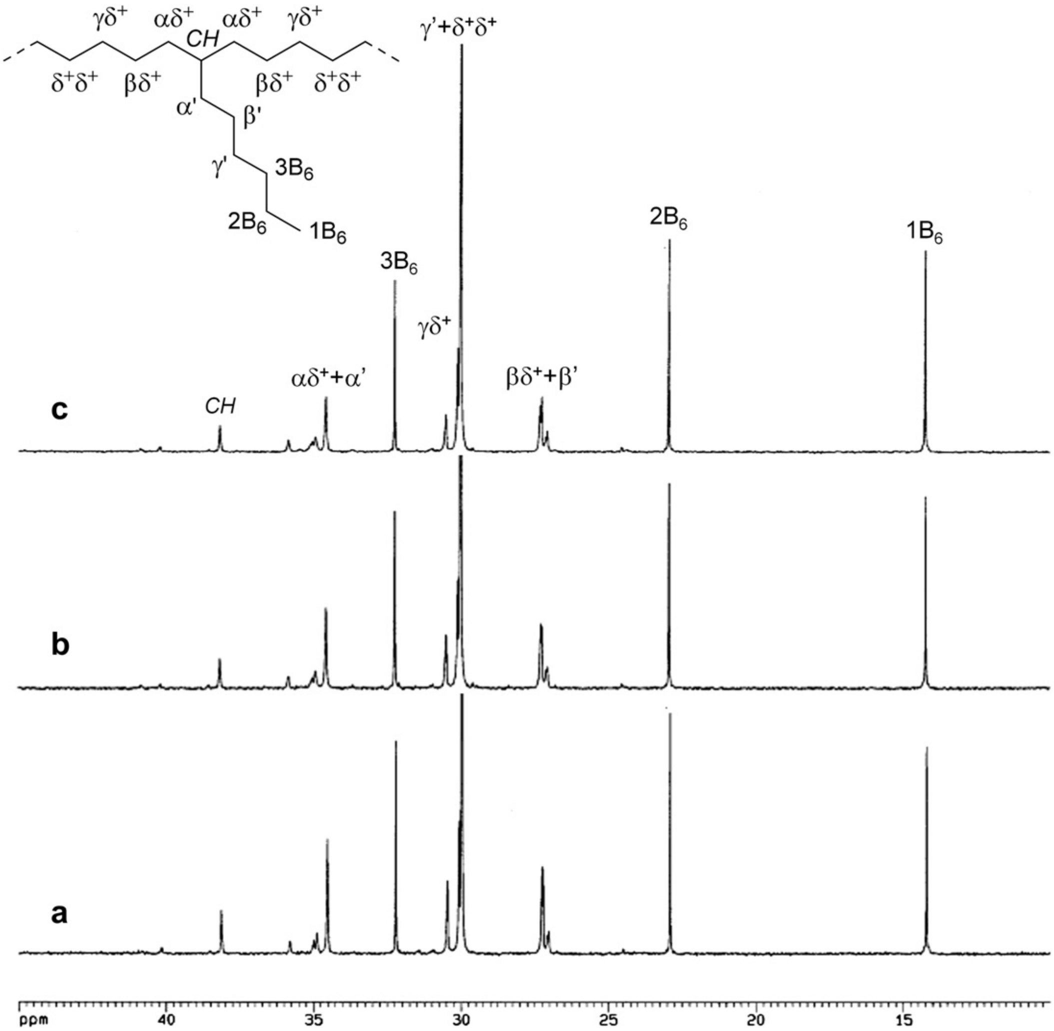


Fig. 3. ^{13}C NMR spectra of poly(ethylene-*co*-1-octene)s at a 1-octene feed of 1.0 mL, from (a) **BPTi$_2$** (run 9), (b) **PhTi$_1$** (run 14), and (c) **MeTi$_1$** (run 18 in Table 1). Peak assignments were made on the carbon atoms contributed from isolated comonomer units.

All these findings appear to be associated with the biphenylene bridge of **BPTi₂** which may lead to not only stabilization of both cationic active centers via a possible electronic conjugation, but also steric isolation of two metal centers provided by rigidity coupled with a proper length. The stabilized cationic metal centers seem to play a key role in slowing down the β–H transfer reactions at the last inserted chain end units against rapid propagation, leading to high molecular weight. The stabilization could also provide high activity at elevated temperature as observed in the ethylene polymerization. On the other hand, the steric isolation may give rise to the equally high (co)monomer insertions at both metal centers, resulting in the similar level of activity and comonomer incorporation compared to those of **PhTi₁**.

The reason for the decrease of activity by **BPTi₂** in comparison with **PhTi₁** at high 1-octene feeds (2.0 and 5.0 mL) is not clear, but it is likely that vinyl-terminated macromonomers formed at one Ti center may interfere with monomer insertion at the proximal Ti. Although a direct evidence of LCB was not detected by ^{13}C NMR analysis of the ethylene homopolymer obtained at 50 °C from **BPTi₂**, facile diffusion of a produced polymer chain to the proximal Ti center due to the enhanced solubility of the copolymer having a high amount of 1-octene appears to lead to such interaction. The similar activity between **BPTi₂** and **PhTi₁** systems in 1-octene homopolymerization (run 12 vs. 17) may plausibly support this assumption because the macromolecular reinsertion process can be actually inhibited in the homopolymerization of large α-olefins such as 1-octene owing to the difficulty in the formation of a vinyl-terminated end group as well as steric hindrance of the growing polymer chain, except for the case of propylene polymerization in which the formation of a vinyl-end group could be possible via β-Me elimination or 2,1-insertion followed by β-H transfer [45].

4. Conclusion

We have prepared a novel permethylated cyclopentadienyl dinuclear Ti-CGC (**BPTi₂**) linked by a rigid biphenylene bridge. **BPTi₂** exhibited high activity and high 1-octene incorporation in ethylene and ethylene/1-octene polymerizations. Particularly, **BPTi₂** led to the significantly increased molecular weight of polymers in both homo- and copolymerization in comparison with those from the corresponding mononuclear Ti-CGC analogs. These results appear to be due to the cooperative participation of the electronic stabilization of two cationic metal centers through the biphenylene group and the isolated ansa-nature of both metal units in **BPTi₂**.

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References

[1] J.H. Park, S.H. Do, A. Cyriac, H. Yun, B.Y. Lee, Dalton Trans. 39 (2010) 9994–10002.
[2] C.J. Wu, S.H. Lee, H. Yun, B.Y. Lee, Organometallics 26 (2007) 6685–6687.
[3] U.G. Joung, C.J. Wu, S.H. Lee, C.H. Lee, E.J. Lee, W.-S. Han, S.O. Kang, B.Y. Lee, Organometallics 25 (2006) 5122–5130.
[4] H. Braunschweig, F.M. Breitling, Coord. Chem. Rev. 250 (2006) 2691–2720.
[5] D.J. Cho, C.J. Wu, S. Sujith, W.-S. Han, S.O. Kang, B.Y. Lee, Organometallics 25 (2006) 2133–2134.
[6] D.J. Joe, C.J. Wu, T. Bok, E.J. Lee, C.H. Lee, W.-S. Han, S.O. Kang, B.Y. Lee, Dalton Trans. (2006) 4056–4062.
[7] V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283–316.
[8] P.S. Chum, W.J. Kruper, M.J. Guest, Adv. Mater. 12 (2000) 1759–1767.
[9] A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587–2598.
[10] S. Bensason, J. Minick, A. Moet, S. Chum, A. Hiltner, E. Baer, J. Polym. Sci., Part B: Polym. Phys. 34 (1996) 1301–1315.
[11] J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Rosen, G.W. Knight, S.Y. Lai, Eur. Pat. Appl. 0,416,815 A2 (1991).
[12] J.A.M. Canich, US Pat. 5,026,798 (1991).
[13] L.J. Irwin, J.H. Reibenspies, S.A. Miller, J. Am. Chem. Soc. 126 (2004) 16716–16717.
[14] P. Walter, S. Trinkle, J. Suhm, D. Mäder, C. Friedrich, R. Mülhaupt, Macromol. Chem. Phys. 201 (2000) 604–612.
[15] W.-J. Wang, E. Kolodka, S. Zhu, A.E. Hamielec, J. Polym. Sci., Part A: Polym. Chem. 37 (1999) 2949–2957.
[16] W.-J. Wang, D. Yan, S. Zhu, A.E. Hamielec, Macromolecules 31 (1998) 8677–8683.
[17] G. Xu, E. Ruckenstein, Macromolecules 31 (1998) 4724–4729.
[18] T.D.H. Nguyen, T.L.T. Nguyen, S.K. Noh, W.S. Lyoo, Polymer 52 (2011) 318–325.
[19] A. Motta, I.L. Fragala, T.J. Marks, J. Am. Chem. Soc. 131 (2009) 3974–3984.
[20] N. Guo, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 130 (2008) 2246–2261.
[21] Y. Zhu, E. Jeong, B. Lee, B. Kim, S. Noh, W. Lyoo, D.-H. Lee, Y. Kim, Macromol. Res. 15 (2007) 430–436.
[22] S.B. Amin, T.J. Marks, J. Am. Chem. Soc. 129 (2007) 2938–2953.
[23] H. Li, L. Li, D.J. Schwartz, M.V. Metz, T.J. Marks, L. Liable-Sands, A.L. Rheingold, J. Am. Chem. Soc. 127 (2005) 14756–14768.
[24] H. Li, C.L. Stern, T.J. Marks, Macromolecules 38 (2005) 9015–9027.
[25] H. Li, L. Li, T.J. Marks, Angew. Chem. Int. Ed. 43 (2004) 4937–4940.
[26] N. Guo, L. Li, T.J. Marks, J. Am. Chem. Soc. 126 (2004) 6542–6543.
[27] J. Wang, H. Li, N. Guo, L. Li, C.L. Stern, T.J. Marks, Organometallics 23 (2004) 5112–5114.
[28] S.K. Noh, M. Lee, D.H. Kum, K. Kim, W.S. Lyoo, D.-H. Lee, J. Polym. Sci., Part A: Polym. Chem. 42 (2004) 1712–1723.
[29] S.K. Noh, Y. Yang, W.S. Lyoo, J. Appl. Polym. Sci. 90 (2003) 2469–2474.
[30] H. Li, L. Li, T.J. Marks, L. Liable-Sands, A.L. Rheingold, J. Am. Chem. Soc. 125 (2003) 10788–10789.
[31] L. Li, M.V. Metz, H. Li, M.-C. Chen, T.J. Marks, L. Liable-Sands, A.L. Rheingold, J. Am. Chem. Soc. 124 (2002) 12725–12741.
[32] S.K. Noh, J. Lee, D.-H. Lee, J. Organomet. Chem. 667 (2003) 53–60.
[33] J. Klosin, W.J. Kruper Jr., P.N. Nickias, G.R. Roof, P. De Waele, K.A. Abboud, Organometallics 20 (2001) 2663–2665.
[34] S.H. Lee, C.J. Wu, U.G. Joung, B.Y. Lee, J. Park, Dalton Trans. (2007) 4608–4614.
[35] S.K. Kim, H.K. Kim, M.H. Lee, S.W. Yoon, Y. Han, S. Park, J. Lee, Y. Do, Eur. J. Inorg. Chem. (2007) 537–545.
[36] M.H. Lee, S.K. Kim, Y. Do, Organometallics 24 (2005) 3618–3620.
[37] J.M. Conia, M.L. Leriverend, Bull. Soc. Chim. Fr. (1970) 2981–2991.
[38] J. Zemánek, P. Štěpnička, K. Fejfarová, R. Gyepes, I. Císařová, M. Horáček, J. Kubišta, V. Varga, K. Mach, Collect. Czech. Chem. Commun. 66 (2001) 605–620.
[39] P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 116 (1994) 4623–4640.
[40] W. Liu, P.L. Rinaldi, L.H. McIntosh, R.P. Quirk, Macromolecules 34 (2001) 4757–4767.
[41] J.C. Randall, J. Macromol. Sci. Rev. Macromol. Chem. Phys. C29 (2&3) (1989) 201–317.
[42] M.F.N.N. Carvalho, K. Mach, A.R. Dias, J.F. Mano, M.M. Marques, A.M. Soares, A.J.L. Pombeiro, Inorg. Chem. Commun. 6 (2003) 331–334.
[43] R. Kravchenko, R.M. Waymouth, Macromolecules 31 (1998) 1–6.
[44] J.C.W. Chien, T. Nozaki, J. Polym. Sci., Part A: Polym. Chem. 31 (1993) 227–237.
[45] A.E. Cherian, E.B. Lobkovsky, G.W. Coates, Macromolecules 38 (2005) 6259–6268.