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

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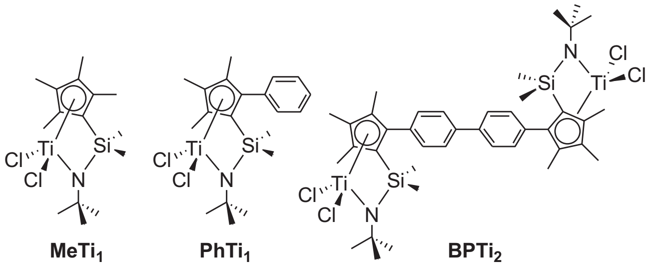
ABSTRACT

Permethylated cyclopentadienyl dinuclear constrained geometry titanium catalyst, $[\mu\text{-}(C_6H_4)_2\text{-}2,2']\{(\eta^5\text{-}C_5Me_3)[1\text{-}Me_2Si(\eta^1\text{-}N\text{-}^tBu)](TiCl_2)\}_2$ (**$BPTi_2$**) 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, $Me_2Si(\eta^5\text{-}2\text{-}PhC_5Me_3)(\eta^1\text{-}N\text{-}^tBu)TiCl_2$ (**$PhTi_1$**) and $Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^1\text{-}N\text{-}^tBu)TiCl_2$ (**$MeTi_1$**), **$BPTi_2$** 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 **$BPTi_2$**.

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 $Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^1\text{-}N\text{-}^tBu)TiCl_2$ (**$MeTi_1$**) 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



$MeTi_1$ **$PhTi_1$** **$BPTi_2$**

Chart 1.

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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], $Me_2Si(\eta^5\text{-2-PhC}_5Me_3)(\eta^1\text{-N-}^t\text{Bu})TiCl_2$ (**PhTi$_1$**) [38], and $Me_2Si(\eta^5\text{-C}_5Me_4)(\eta^1\text{-N-}^t\text{Bu})TiCl_2$ (**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, $C_6\mathit{H}_4$), 7.40 (d, 4H, $C_6\mathit{H}_4$), 3.22 (s, 4H, $C_5Me_3\mathit{H}_2$), 2.11 (s, 6H, $C_5\mathit{Me}_3H_2$), 2.00 (s, 6H, $C_5\mathit{Me}_3H_2$), 1.87 (s, 6H, $C_5\mathit{Me}_3H_2$). ^{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 ($C_5\mathit{Me}_3$), 13.29 ($C_5\mathit{Me}_3$), 11.24 ($C_5\mathit{Me}_3$). 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 $[2,2'\text{-}(C_6H_4)_2][1\text{-}Me_2Si(NH\text{-}^t\text{Bu})(C_5Me_3H)]_2$ **(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, $C_6\mathit{H}_4$), 7.29 (d, 4H, $C_6\mathit{H}_4$), 3.81 (s, 2H, $C_5Me_3\mathit{H}$), 2.15 (s, 6H, $C_5\mathit{Me}_3H$), 2.08 (s, 6H, $C_5\mathit{Me}_3H$), 1.93 (s, 6H, $C_5\mathit{Me}_3H$), −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 ($Si\mathit{C}_5Me_3$), 14.74 ($C_5\mathit{Me}_3$), 12.86 ($C_5\mathit{Me}_3$), 11.22 ($C_5\mathit{Me}_3$), 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 $^t\text{BuNH}_2$ (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, $C_6\mathit{H}_4$), 7.28 (d, 4H, $C_6\mathit{H}_4$), 3.59 (s, 2H, $C_5Me_3\mathit{H}$), 2.08 (s, 6H, $C_5\mathit{Me}_3H$), 2.05 (s, 6H, $C_5\mathit{Me}_3H$), 1.90 (s, 6H, $C_5\mathit{Me}_3H$), 0.94 (s, 18H, $NHC\mathit{Me}_3$), 0.32 (s, 2H, $N\mathit{H}CMe_3$), −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 ($N\mathit{C}Me_3$), 49.24 ($Si\mathit{C}_5Me_3$), 33.49 ($NC\mathit{Me}_3$), 15.06 ($C_5\mathit{Me}_3$), 12.66 ($C_5\mathit{Me}_3$), 11.18 ($C_5\mathit{Me}_3$), 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 $[\mu\text{-}(C_6H_4)_2\text{-}2,2']\{(\eta^5\text{-}C_5Me_3)[1\text{-}Me_2Si(\eta^1\text{-}N\text{-}^t\text{Bu})](TiCl_2)\}_2$ **(BPTi$_2$)**

A solution of 2.50 g of $[2,2'\text{-}(C_6H_4)_2][1\text{-}Me_2Si(NH\text{-}^t\text{Bu})(C_5Me_3H)]_2$ (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