

## Article

# Syntheses of Silylene-Bridged Thiophene-Fused Cyclopentadienyl *ansa*-Metallocene Complexes for Preparing High-Performance Supported Catalyst

Sun Mi Jeong <sup>1</sup>, Ju Yong Park <sup>1</sup>, Yong Bin Hyun <sup>1</sup>, Jun Won Baek <sup>1</sup> , Hagjun Kim <sup>2</sup>, Yeokwon Yoon <sup>2</sup>, Sangchul Chung <sup>2</sup>, Junseong Lee <sup>3</sup>  and Bun Yeoul Lee <sup>1,\*</sup> 

<sup>1</sup> Department of Molecular Science and Technology, Ajou University, Suwon 16499, Korea; sunmi7523@ajou.ac.kr (S.M.J.); pjy3741@ajou.ac.kr (J.Y.P.); ybh0221@ajou.ac.kr (Y.B.H.); btw91@ajou.ac.kr (J.W.B.)

<sup>2</sup> Olefins Technology Team, GS Caltex R&D Center, Daejeon 34122, Korea; khjun@gscaltex.com (H.K.); yeokwon@gscaltex.com (Y.Y.); topiron@gscaltex.com (S.C.)

<sup>3</sup> Department of Chemistry, Chonnam National University, Gwangju 61186, Korea; leespy@chonnam.ac.kr

\* Correspondence: bunyeoul@ajou.ac.kr; Tel.: +82-31-219-1844

**Abstract:** We synthesized a series of Me<sub>2</sub>Si-bridged *ansa*-zirconocene complexes coordinated by thiophene-fused cyclopentadienyl and fluorenyl ligands (Me<sub>2</sub>Si(2-R<sup>1</sup>-3-R<sup>2</sup>-4,5-Me<sub>2</sub>C<sub>7</sub>S)(2,7-R<sup>3</sup><sub>2</sub>C<sub>13</sub>H<sub>6</sub>)) ZrMe<sub>2</sub> (R<sup>1</sup> = Me or H, R<sup>2</sup> = H or Me, R<sup>3</sup> = H, tBu, or Cl) for the subsequent preparation of supported catalysts. We determined that the fluorenyl ligand adopts an η<sup>3</sup>-binding mode in **9** (R<sup>1</sup> = Me, R<sup>2</sup> = H, R<sup>3</sup> = H) by X-ray crystallography. Further, we synthesized a derivative **15** by substituting the fluorenyl ligand in **9** with a 2-methyl-4-(4-*tert*-butylphenyl)indenyl ligand, derivatives **20** and **23** by substituting the Me<sub>2</sub>Si bridge in **12** (R<sup>1</sup> = Me, R<sup>2</sup> = H, R<sup>3</sup> = tBu) and **15** with a tBuO(CH<sub>2</sub>)<sub>6</sub>(Me)Si bridge, and the dinuclear congener **26** by connecting two complexes with a -(Me)Si(CH<sub>2</sub>)<sub>6</sub>Si(Me)- spacer. The silica-supported catalysts prepared using **12**, **20**, and **26** demonstrated up to two times higher productivity in ethylene/1-hexene copolymerization than that prepared with conventional (THI)ZrCl<sub>2</sub> (**21–26** vs. 12 kg-PE/g-(supported catalyst)), producing polymers with comparable molecular weight (M<sub>w</sub>, 330–370 vs. 300 kDa), at a higher 1-hexene content (1.3 vs. 1.0 mol%) but a lower bulk density of polymer particles (0.35 vs. 0.42 g/mL).

**Keywords:** metallocene catalyst; supported catalyst; thiophene-fused cyclopentadienyl; ethylene polymerization



**Citation:** Jeong, S.M.; Park, J.Y.; Hyun, Y.B.; Baek, J.W.; Kim, H.; Yoon, Y.; Chung, S.; Lee, J.; Lee, B.Y. Syntheses of Silylene-Bridged Thiophene-Fused Cyclopentadienyl *ansa*-Metallocene Complexes for Preparing High-Performance Supported Catalyst. *Catalysts* **2022**, *12*, 283. <https://doi.org/10.3390/catal12030283>

Academic Editor: Francisco J. Fernández-Alvarez

Received: 4 February 2022

Accepted: 28 February 2022

Published: 2 March 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



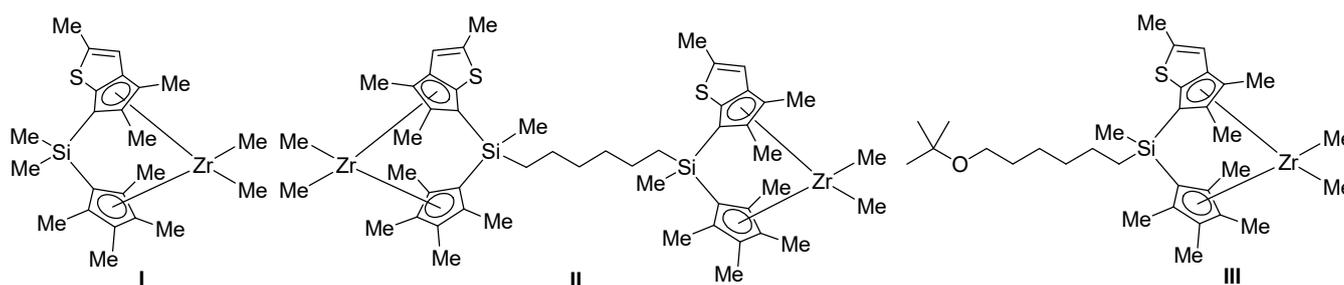
**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Homogeneous single-site catalysts, such as metallocene and half-metallocene, and post-metallocene catalysts are actively used in the production of polyethylene (PE) and polypropylene (PP), although most PE and PP is still produced by using heterogeneous Ziegler–Natta catalysts [1,2]. While homogeneous catalysts can be directly used in a solution process where polymers (e.g., polyolefin elastomer (POE) with high α-olefin content) are formed by dissolution in solvent, they should be immobilized on an inorganic support, e.g., silica, in order to be applied in a slurry-process or a gas-phase process, where the morphology of the generated polymer particles is of importance for stable operation [3–11]. When a homogeneous catalyst is injected, as dissolved, into a slurry- or gas-phase reactor, the shape and size of the generated polymer particles are irregularly uncontrolled, making stable operation impossible (termed ‘fouling’) as well as causing low productivity due to low bulk density. Because a large portion of PE and PP is produced by the slurry and gas-phase processes, high-performance supported catalysts are essential in the industrial sector [12–26].

Recently, we reported the syntheses of *ansa*-metallocene complexes coordinated by thiophene-fused cyclopentadienyl and tetramethylcyclopentadienyl ligands (**I** in Scheme 1),

the dinuclear congener (II), and its analog attaching the  $t\text{BuO}(\text{CH}_2)_6$ -tether (III), where we showed that the supported catalysts of II and III outperformed those prepared with I, exhibiting the same activity as when dissolved in the homogeneous phase [27]. Other studies also reported the syntheses of metallocene and half-metallocene complexes with thiophene-fused cyclopentadienyl ligands (some of which have been used for commercial processes with advantageous performance) [28–33] and the syntheses of dinuclear complexes, for the purpose of developing new polymerization catalysts [34–40]. In this work, we synthesized a series of silylene-bridged *ansa*-metallocene complexes constructed with thiophene-fused cyclopentadienyl ligands for the purpose of preparing high-performance supported catalysts, the successful results of which are reported herein.

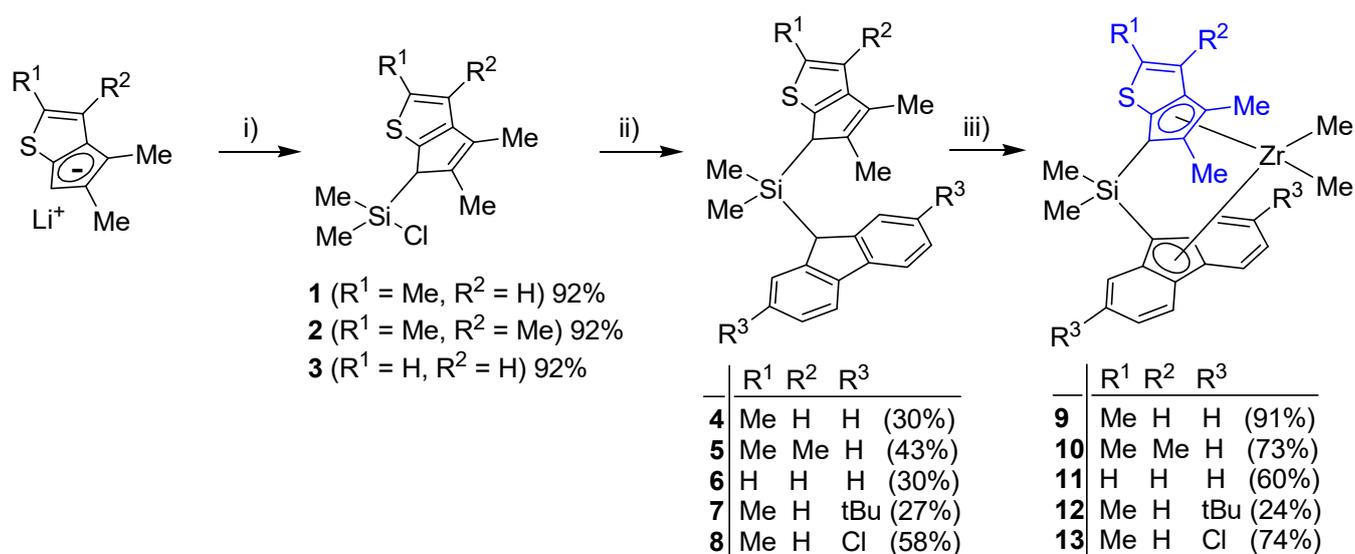


**Scheme 1.** Mononuclear (I), dinuclear (II), and  $t\text{BuO}(\text{CH}_2)_6$ -tether containing (III) *ansa*-metallocene complexes synthesized with thiophene-fused cyclopentadienyl ligands.

## 2. Results and Discussion

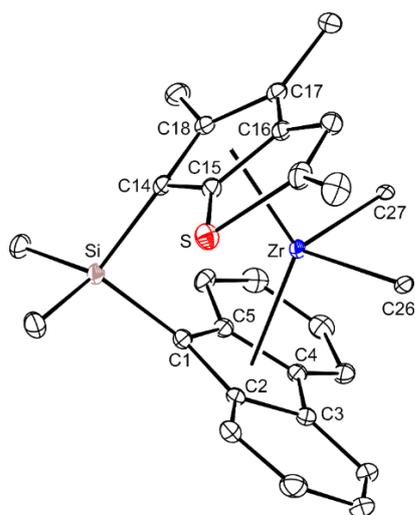
### 2.1. Preparation of *ansa*-Metallocene Complexes

First, we discuss the syntheses of  $\text{Me}_2\text{Si}$ -bridged *ansa*-zirconocene complexes coordinated by a thiophene-fused cyclopentadienyl and a fluorenyl ligand (Scheme 2). We substituted the expensive tetramethylcyclopentadienyl ligands in I–III with fluorenyl ligands. We prepared the thiophene-fused cyclopentadiene compounds on a large scale (50 g scale with 1 L glassware) [41,42]. The treatment of  $n\text{BuLi}$  with thiophene-fused cyclopentadiene compounds in hexane precipitated the corresponding cyclopentadienyl–Li salt in ~90% yield. The addition of excess  $\text{Me}_2\text{SiCl}_2$  (3.0 eq) to the Li salts in toluene produced  $\text{Me}_2(\text{Cl})\text{Si}$ -attached compounds 1–3. The treatment of 1–3 with fluorenyl–Li produced the target compounds 4–8 in yields ranging from 27% to 58%. We removed all unidentified side products via column chromatography and purified the obtained products via recrystallization in hexane at  $-30\text{ }^\circ\text{C}$ . We performed the metalation according to the following established synthetic protocol: lithiation with 2.0 eq  $n\text{BuLi}$  in THF, followed by the sequential addition of  $\text{MeMgBr}$  (2.3 eq) and  $\text{ZrCl}_4 \cdot (\text{THF})_2$  (0.98 eq) [43,44]. The target *ansa*-zirconocene complexes 9–13 were isolated via toluene extraction and purified by precipitation in toluene at  $-30\text{ }^\circ\text{C}$ . Except for the 2,7-di(*tert*-butyl)fluorenyl ligand-containing 12 (24% yield), the metalation produced all the target complexes with good yields ranging from 60% to 91%. The  $^1\text{H}$  NMR spectra of 9–13 showed two diastereotopic  $\text{Zr}-\text{CH}_3$  signals at  $-1.6$  and  $-1.1$  ppm as singlets. Small variations in the chemical shifts were caused by different substituents in the thiophene ring and fluorenyl ligand (Figures S9–S13). The  $^1\text{H}$  NMR spectra also showed two diastereotopic Si-bound methyl group signals at 1.04–1.08 ppm and 0.82–0.84 ppm for 9–11, at 1.16 and 0.98 ppm for 12 (downfield shifts caused by electron-donating *t*Bu groups), and at 0.89 and 0.67 ppm for 13 (upfield shifts caused by electron-withdrawing Cl groups).



**Scheme 2.** Syntheses of  $\text{Me}_2\text{Si}$ -bridged *ansa*-zirconocene complexes coordinated by thiophene-fused cyclopentadienyl and fluorenyl ligands: (i)  $\text{Me}_2\text{SiCl}_2$  in toluene, (ii) 2,7- $\text{R}^3$ -fluorenyl-Li in THF, (iii)  $n\text{BuLi}$  (2.0 eq) in THF and then addition of  $\text{MeMgBr}$  (2.3 eq) and  $\text{ZrCl}_4 \cdot (\text{THF})_2$ .

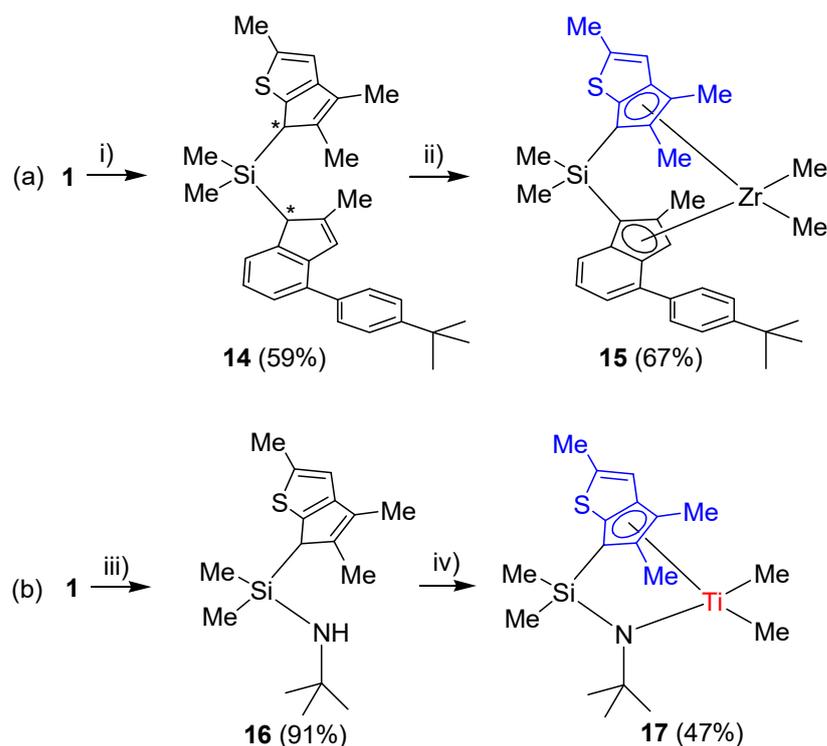
Because the solids precipitated in toluene were not suitable for X-ray crystallography, we grew single crystals of **9** in a  $\text{CH}_2\text{Cl}_2$  solution via the slow evaporation of  $\text{CH}_2\text{Cl}_2$  in a closed chamber containing methylcyclohexane. The bond lengths measured by X-ray crystallography suggested an  $\eta^3$ -binding mode for the fluorenyl ligand and an  $\eta^5$ -binding mode for the thiophene-fused cyclopentadienyl ligand; the two Zr-C bonds in the fluorenyl ligand (Zr-C3, 2.8122(31) Å and Zr-C4, 2.807(3) Å) were too long to be considered chemical bonds (Figure 1). The closest Zr-C distance in the fluorenyl ligand (i.e., Zr-C1, 2.438(3) Å) was shorter than that in the thiophene-fused cyclopentadienyl ligand (i.e., Zr-C14, 2.485(3) Å). The bridged Si atom was located slightly out of the plane formed by either the fluorenyl ligand or the thiophene-fused cyclopentadienyl ligand (Si-C14-centroid of C14-C15-C16-C17-C18 ring, 159.2°; Si-C1-centroid of C1-C2-C3-C4-C5 ring, 168.2°).



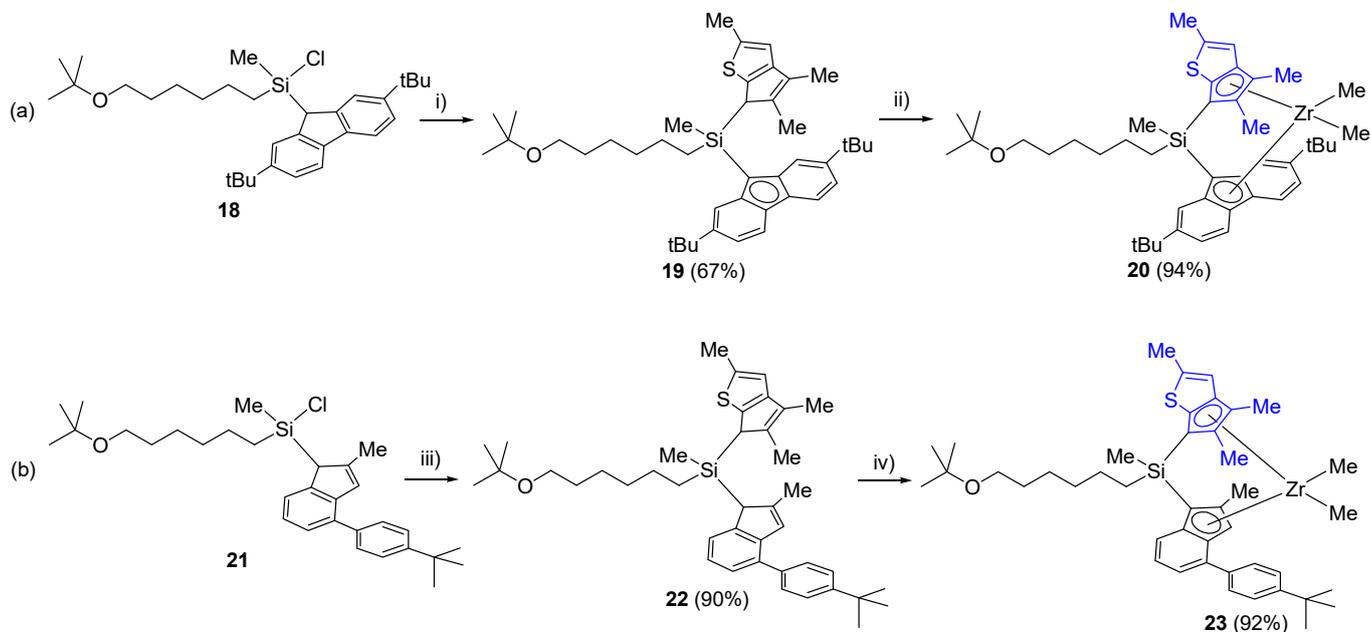
**Figure 1.** Thermal ellipsoid plot (30% probability level) of **9**. Selected bond distances (Å) and angles (°): Zr-C1, 2.438(3); Zr-C2, 2.587(3); Zr-C3, 2.812(31); Zr-C4, 2.807(3); Zr-C5, 2.571(3); Zr-C14, 2.485(3); Zr-C15, 2.513(3); Zr-C16, 2.614(3); Zr-C17, 2.589(3); Zr-C18, 2.502(3); Zr-C26, 2.261(10); Zr-C27, 2.336(3); C1-C2, 1.461(4); C1-C5, 1.445(4); C2-C3, 1.434(4); C4-C5, 1.435(4); C3-C4, 1.439(4); C14-C15, 1.432(4); C14-C18, 1.443(4); C15-C16, 1.420(4); C17-C18, 1.429(4); C16-C17, 1.421(4); C1-Si-C14, 97.05(12); Si-C1-Zr, 97.51(11); Si-C14-Zr, 95.72(11); C26-Zr-C27, 93.90(3).

Next, we discuss the syntheses of Me<sub>2</sub>Si-bridged *ansa*-zirconocene complexes coordinated by a thiophene-fused cyclopentadienyl ligand and a 2-methyl-4-(4-*tert*-butylphenyl)indenyl ligand (Scheme 3). The reaction of 2-methyl-4-(4-*tert*-butylphenyl)indenyl–Li with Me<sub>2</sub>(Cl)Si-attached thiophene-fused cyclopentadiene compound **1** produced the target ligand precursor **14** in 59% yield. The metalation of **14** afforded the Me<sub>2</sub>Si-bridged *ansa*-zirconocene complex **15** coordinated by thiophene-fused cyclopentadienyl and 2-methyl-4-(4-*tert*-butylphenyl)indenyl ligands in 67% yield (Scheme 3a). The <sup>1</sup>H NMR spectrum of **14** showed two sets of signals attributed to the presence of two diastereomers. The intensities of the minor set were low (1.0:0.11), indicating that the formation of one of the diastereomers was not favored. The <sup>1</sup>H NMR spectrum of **15** also showed two sets of signals attributed to the presence of two diastereomers—racemic-type and meso-type forms; however, the highly biased ratio (i.e., 1.0:0.11) observed for ligand precursor **14** was lost in the deprotonation steps and it changed to a less biased 1.0:0.54 (or vice versa) after metalation. The singlet Zr–CH<sub>3</sub> and Si–CH<sub>3</sub> signals were observed at –0.86, –0.37, 0.74, and 0.78 ppm for one diastereomer and at –1.32, 0.17, 0.35, and 0.62 ppm for the other diastereomer (Figure S15). Attempts to separate the two isomers via recrystallization using various methods and conditions were unsuccessful. The <sup>1</sup>H NMR spectrum of the toluene extract showed broad signals at 3.77 and 1.37 ppm along with those assigned to the product; we attributed these signals to MgCl<sub>2</sub>·(THF) byproducts. According to previous studies, these THF signals could be completely removed either by the recrystallization process, as in the synthesis of **9–13**, or by the hexane extraction process once the complex dissolved in hexane. However, because **15** could neither be crystallized in toluene nor was soluble in hexane, the complete removal of THF signals was not possible. As they contained MgCl<sub>2</sub> impurity, the elemental analysis data of **15** were not in agreement. Even for **9–13**, which were purified by crystallization in toluene removing the THF signals almost completely, MgCl<sub>2</sub> impurity might not have been thoroughly removed; the carbon contents measured in the elemental analyses were several % less than the calculated values. We prepared the CGC-type titanium complex **17** coordinated by a thiophene-fused cyclopentadienyl ligand according to the routine method (Scheme 3b).

Next, we discuss the syntheses of *ansa*-metallocene complexes attaching a tBuO(CH<sub>2</sub>)<sub>6</sub>-tether (Scheme 4). Metallocene complexes attaching tBuO(CH<sub>2</sub>)<sub>6</sub>-tether have been routinely used in the preparation of high-performance supported catalysts with some advantages (proprietary catalysts for LG Chem) [11,45]. In the same way, we prepared *ansa*-metallocene complexes attaching tBuO(CH<sub>2</sub>)<sub>6</sub>-tether by replacing the Me<sub>2</sub>Si bridge with a tBuO(CH<sub>2</sub>)<sub>6</sub>(Me)Si bridge. The reaction of the thiophene-fused cyclopentadienyl–Li ((Me<sub>3</sub>C<sub>7</sub>H<sub>2</sub>S)<sup>–</sup>Li<sup>+</sup>) with 1.0 eq tBuO(CH<sub>2</sub>)<sub>6</sub>(Me)SiCl<sub>2</sub> in THF furnished the target compound tBuO(CH<sub>2</sub>)<sub>6</sub>(Me)Si(Cl)(Me<sub>3</sub>C<sub>7</sub>H<sub>2</sub>S); however, the formation of a side product, i.e., dialkylated compound tBuO(CH<sub>2</sub>)<sub>6</sub>(Me)Si(Me<sub>3</sub>C<sub>7</sub>H<sub>2</sub>S)<sub>2</sub> was observed. Unlike the synthesis of **1** (Me<sub>2</sub>Si(Cl)(Me<sub>3</sub>C<sub>7</sub>H<sub>2</sub>S)), where excess Me<sub>2</sub>SiCl<sub>2</sub> (3.0 eq) could react with (Me<sub>3</sub>C<sub>7</sub>H<sub>2</sub>S)<sup>–</sup>Li<sup>+</sup> to avoid the formation of the dialkylated compound Me<sub>2</sub>Si(Me<sub>3</sub>C<sub>7</sub>H<sub>2</sub>S)<sub>2</sub>, excess tBuO(CH<sub>2</sub>)<sub>6</sub>(Me)SiCl<sub>2</sub> could not be added in the synthesis of tBuO(CH<sub>2</sub>)<sub>6</sub>(Me)Si(Cl)(Me<sub>3</sub>C<sub>7</sub>H<sub>2</sub>S) because the removal of the unreacted tBuO(CH<sub>2</sub>)<sub>6</sub>(Me)SiCl<sub>2</sub> would be difficult. Therefore, the formation of the dialkylated side product tBuO(CH<sub>2</sub>)<sub>6</sub>(Me)Si(2,7-*t*Bu<sub>2</sub>C<sub>13</sub>H<sub>7</sub>)<sub>2</sub> was inevitable in the reaction of 2,7-di-*tert*-butylfluorenyl–Li ((2,7-*t*Bu<sub>2</sub>C<sub>13</sub>H<sub>7</sub>)<sup>–</sup>Li<sup>+</sup>) with 1.0 eq tBuO(CH<sub>2</sub>)<sub>6</sub>(Me)SiCl<sub>2</sub> performed in THF. We circumvented this problem by reacting (2,7-*t*Bu<sub>2</sub>C<sub>13</sub>H<sub>7</sub>)<sup>–</sup>Li<sup>+</sup> with 1.0 eq tBuO(CH<sub>2</sub>)<sub>6</sub>(Me)SiCl<sub>2</sub> in hexane with a small amount of *tert*-butyl methyl ether (3.3 eq/Li<sup>+</sup>) and at low temperature (–78 °C). This approach gave the target monoalkylated compound **18** with a negligible amount of dialkylated side product tBuO(CH<sub>2</sub>)<sub>6</sub>(Me)Si(2,7-*t*Bu<sub>2</sub>C<sub>13</sub>H<sub>7</sub>)<sub>2</sub> (ca., 1 mol%, Figure S18, Scheme 4a) [46]. We noted that this approach did not work for fluorenyl–Li without the bulky *t*Bu substituents (e.g., (C<sub>13</sub>H<sub>9</sub>)<sup>–</sup>Li<sup>+</sup>), as the dialkylated side product (tBuO(CH<sub>2</sub>)<sub>6</sub>(Me)Si(fluorenyl)<sub>2</sub>) was produced at a substantial amount (10 mol%).

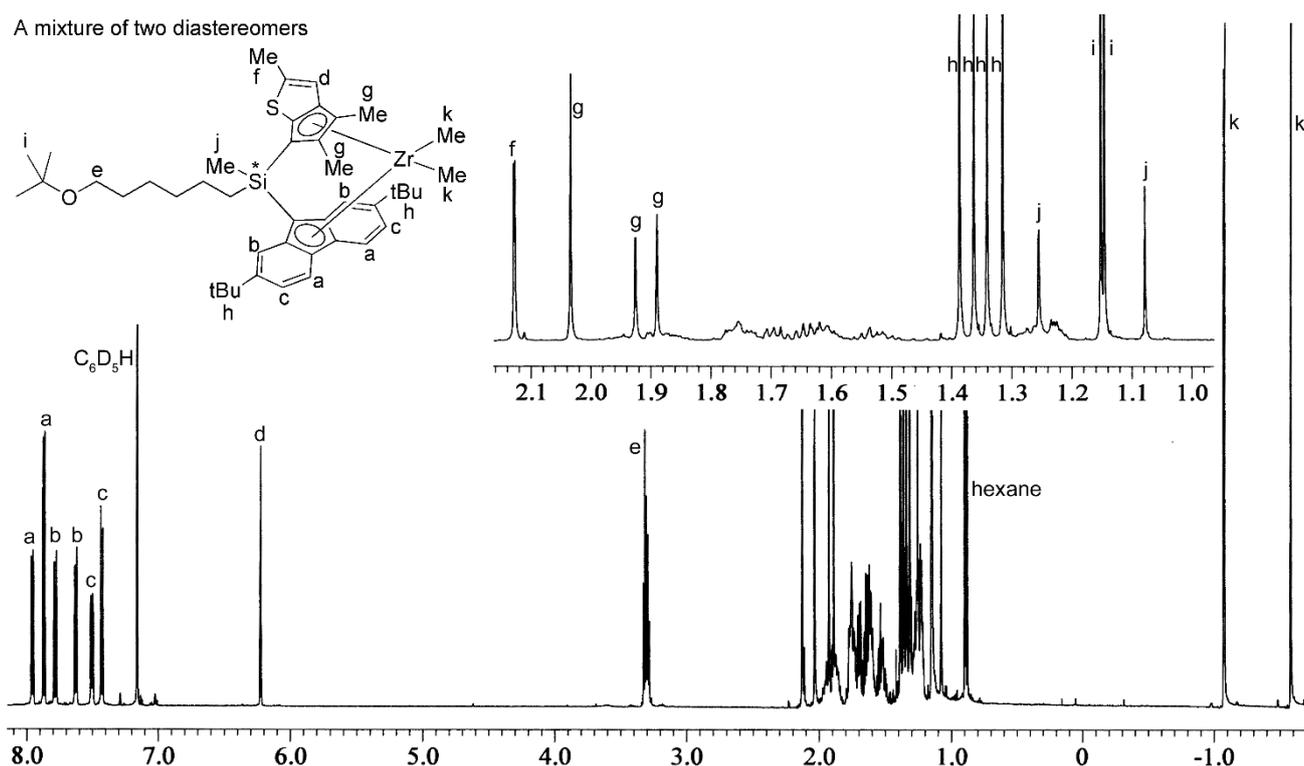


**Scheme 3.** Syntheses of *ansa*-zirconocene complex coordinated by thiophene-fused cyclopentadienyl and a 2-methyl-4-(4-*tert*-butylphenyl)indenyl ligand (a) (asterisks for chiral centers) or a CGC-type titanium complex (b): (i) 2-Methyl-4-(4-*tert*-butylphenyl)indenyl-Li in THF, (ii) nBuLi (2.0 eq) in THF and then addition of MeMgBr (2.3 eq) and ZrCl<sub>4</sub>·(THF)<sub>2</sub>, (iii) *tert*-BuN(H)Li in THF, (iv) nBuLi (2.0 eq) in THF and then addition of MeMgBr (2.1 eq) and TiCl<sub>4</sub>·DME.



**Scheme 4.** Syntheses of 2,7-di-*tert*-butylfluorenyl *ansa*-metallocene complex attaching tBuO(CH<sub>2</sub>)<sub>6</sub>-tether (a) and 2-methyl-4-(4-*tert*-butylphenyl)indenyl *ansa*-metallocene complex attaching tBuO(CH<sub>2</sub>)<sub>6</sub>-tether (b): (i) 2,7-(*t*Bu)<sub>2</sub>-fluorenyl-Li in THF, (ii) nBuLi (2.0 eq) in THF and then addition of MeMgBr (2.3 eq) and ZrCl<sub>4</sub>·(THF)<sub>2</sub>, (iii) 2-methyl-4-(4-*tert*-butylphenyl)indenyl-Li in THF, (iv) nBuLi (2.0 eq) in THF and then addition of MeMgBr (2.3 eq) and ZrCl<sub>4</sub>·(THF)<sub>2</sub>.

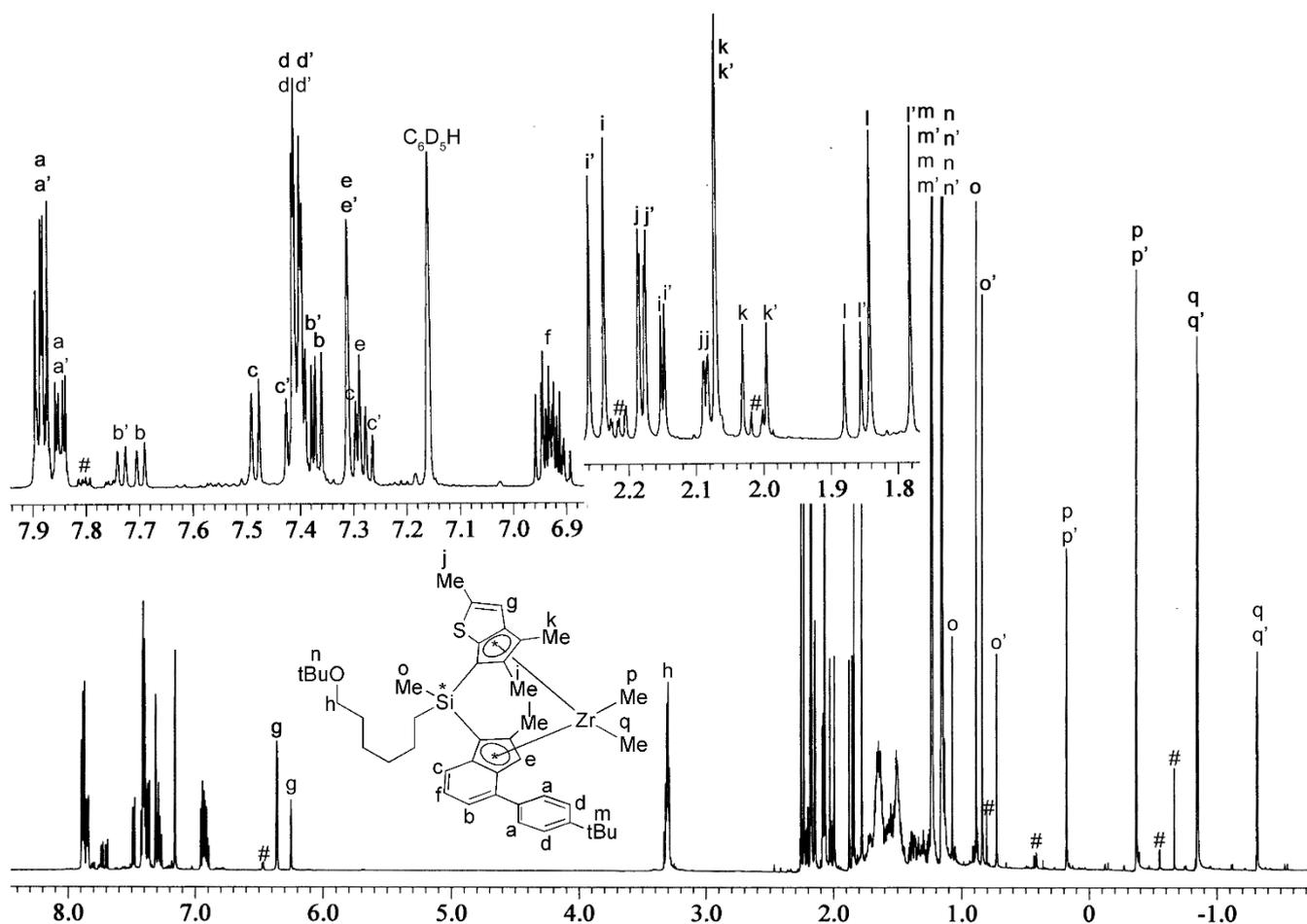
The reaction of the thiophene-fused cyclopentadienyl-K  $((\text{Me}_3\text{C}_7\text{H}_2\text{S})^- \text{K}^+)$  with **18** produced the target compound **19** in 67% yield. The metalation of **19** produced the target *ansa*-metallocene complex **20** containing  $\text{tBuO}(\text{CH}_2)_6$ -tether in 94% yield. The presence of this tether rendered **20** soluble in hexane, which enabled the purification via hexane extraction. The  $^1\text{H}$  NMR spectrum of the purified **20** showed no THF signal (Figure 2), and the compound was used without further purification in the preparation of the supported catalyst. There were two diastereomers in **20** due to a chiral center on Si atom and a plane chirality on thiophene-fused cyclopentadienyl ligand. However, most of signals were not split by the diastereomerism, or were split very narrowly, allowing signal assignment; only Si- $\text{CH}_3$  signal was split widely at 1.08 and 1.26 ppm (Figure 2).



**Figure 2.**  $^1\text{H}$  NMR spectrum of **20** (asterisk for chiral center).

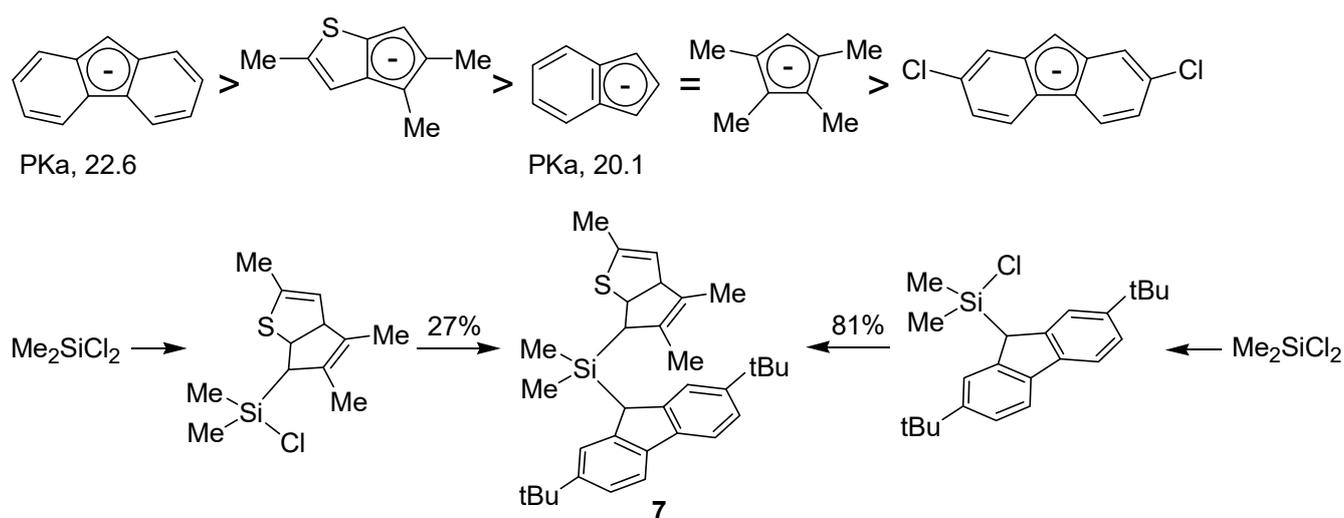
The reaction of 2-methyl-4-(4-*tert*-butylphenyl)indenyl-Li and 1.0 eq  $\text{tBuO}(\text{CH}_2)_6(\text{Me})\text{SiCl}_2$  in hexane in the presence of a small amount of *tert*-butyl methyl ether (3.3 eq/Li $^+$ ) at  $-78^\circ\text{C}$  produced the target compound **21** without the formation of dialkylated species (Scheme 4b). The  $^1\text{H}$  NMR spectrum of **21** indicated a 1:0.7 diastereomeric mixture (Figure S20). The reaction of the thiophene-fused cyclopentadienyl-K  $((\text{Me}_3\text{C}_7\text{H}_2\text{S})^- \text{K}^+)$  with **21** in THF afforded the target compound **22** in 90% yield. The  $^1\text{H}$  NMR spectrum of **22** was too complicated to be clearly assigned due to the presence of three chiral centers (Figure S21). The metalation of **22** gave the target *ansa*-metallocene complex **23** in 92% yield. The  $^1\text{H}$  NMR spectrum of **23** purified by hexane extraction could be interpreted as a mixture of racemic-type and meso-type complexes in 1.0:0.40 ratio (or vice versa), each of which was further split into a 1:0.9 and 1:1 ratio, respectively, due to the additional chiral centers on the Si atoms for a total of four diastereomers (Figure 3). The  $^1\text{H}$  NMR signals of the two methyl groups bonded to Zr ( $\text{Zr}-\text{CH}_3$ ) were observed at  $-0.85$  ppm (narrowly split by a chirality on the Si atom) and at  $-0.37$  ppm for the racemic-type complex. Another set of  $\text{Zr}-\text{CH}_3$  signals was observed at  $-1.32$  ppm (narrowly split by a chirality on Si atom) and at  $0.18$  ppm for the minor meso-type complex. For the racemic-type complex, two Si- $\text{CH}_3$  signals were observed, at  $0.84$  and  $0.88$  ppm (1:0.9 ratio), due to the diastereomerism on the Si atom, while two Si- $\text{CH}_3$  signals were observed, at  $0.73$  and  $1.07$  ppm (1:1 ratio), for the

meso-type complex as well. During the hexane extraction, the  $MgCl_2$  impurities seemed to be almost completely removed, and the elemental analysis data of **20** and **23** as forms of hexane extract only were quite in agreement with the calculated values, although the carbon contents were still somewhat deviated by 1.2–1.3%.



**Figure 3.**  $^1H$  NMR spectrum of **23**. Racemic-type and meso-type complexes in 1:0.4 ratio (or vice versa) are further split in 1:0.9 and 1:1 ratios, respectively, which are assigned as *o*, *o'*, *o*, and *o'*, for example, for Si-CH<sub>3</sub> signals. Signals for unidentified impurities are marked with # and the chiral centers are marked with asterisks.

Next, we discuss the yield improvement of compounds **4–7** by reaction-sequence reversal (Scheme 5). The yields in the syntheses of **4–7** were lower (27–43%) compared to that in the synthesis of **19** (67%). The difference between the two processes is the respective reaction sequences involving  $Me_2SiCl_2$  and  $tBuO(CH_2)_6(Me)SiCl_2$ . For **4–7**, the thiophene-fused cyclopentadienyl-Li first reacted with  $Me_2SiCl_2$  before reacting with fluorenyl-Li, whereas for **19**, the fluorenyl-Li first reacted with  $tBuO(CH_2)_6(Me)SiCl_2$  before reacting with the thiophene-fused cyclopentadienyl-K. We attribute the low yields of **4–7** to the deprotonation of the  $Me_2(Cl)Si$ -attached thiophene-fused cyclopentadiene compounds **1–3** by the action of the basic fluorenyl anion. By  $^1H$  NMR analysis, we determined the following basicity sequence:

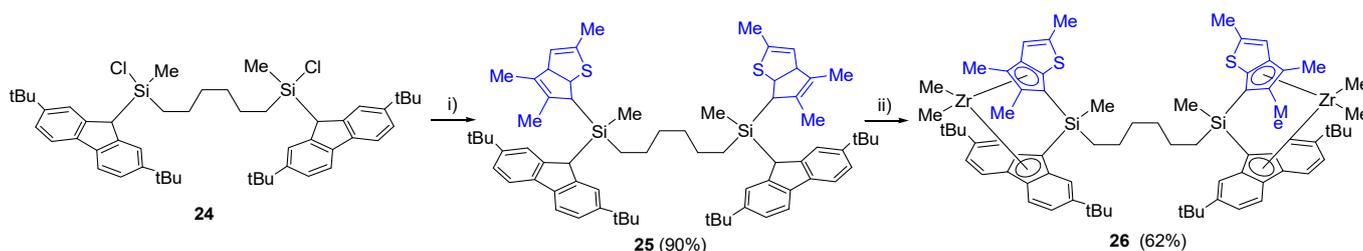


**Scheme 5.** Basicity order derived from  $^1\text{H}$  NMR studies (**top**) and the yield improvement by reversing the reaction sequence (**bottom**).

Fluorenyl-Li (pKa, 22.6) > thiophene-fused cyclopentadienyl-Li ( $(\text{Me}_3\text{C}_7\text{H}_2\text{S})^- \text{Li}^+$ ) > indenyl-Li (pKa, 20.1)  $\approx$  tetramethylcyclopentadienyl-Li > 2,7-dichlorofluorenyl-Li (Scheme 5, top panel).

This sequence could be inferred from the observations that in THF- $d^8$ ,  $(\text{Me}_3\text{C}_7\text{H}_2\text{S})^- \text{Li}^+$  could deprotonate indene, tetramethylcyclopentadiene, and 2,7-dichlorofluorene but not fluorene. Further, while the reaction of 2,7-dichlorofluorene with tetramethylcyclopentadienyl-Li produced 2,7-dichlorofluorenyl-Li, the reaction of indenyl-Li with tetramethylcyclopentadiene produced solid deposits of tetramethylcyclopentadienyl-Li with the formation of indene, reaching an equilibrium at  $\sim 60\%$  conversion. Following these observations, we reversed the reaction sequence, first by reacting the more basic fluorenyl-Li with  $\text{Me}_2\text{SiCl}_2$ , followed by the less basic thiophene-fused cyclopentadienyl-Li. This sequence reversal improved the yield of **7** dramatically from 27% to 81% (Scheme 5, bottom panel).

Next, we discuss the syntheses of dinuclear *ansa*-zirconocene complexes (Scheme 6). Various dinuclear *ansa*-metallocene complexes were synthesized with silylene-bridged cyclopentadienyl, indenyl, or fluorenyl ligands in the early 2000s, demonstrating higher activity than the mononuclear congener [47,48]. We also demonstrated that dinuclear complexes of thiophene-fused cyclopentadienyl and tetramethylcyclopentadienyl ligands could be used in the preparation of supported catalysts with some advantages. For example, a higher amount of complexes could be anchored on the support, thus achieving higher activity and obtaining finer polymer particles [27]. We prepared **24**, the dinuclear complexes of silylene-bridged *ansa*-zirconocene complexes coordinated with thiophene-fused cyclopentadienyl and 2,7-di(*tert*-butyl)fluorenyl ligands with an optimal hexamethylene  $(-\text{Me})\text{Si}(\text{CH}_2)_6\text{Si}(\text{Me})-$  spacer (Scheme 6). The reaction of **24** via the reversed sequence mentioned above afforded the ligand precursor **25** in 90% yield. The metalation of **25** gave the target dinuclear complex **26** in 62% yield. Since complex **26** was soluble in hexane, a fairly pure complex was obtained, with the complete removal of the contaminant THF signals in the  $^1\text{H}$  NMR spectrum. The signals were split due to the chiral centers on the Si atom, but the splitting was so narrow that the peaks could be unambiguously interpreted (Figure S24).



**Scheme 6.** Syntheses of dinuclear *ansa*-zirconocene complexes: (i) (2,4,5-Me<sub>3</sub>C<sub>7</sub>H<sub>2</sub>S)K in THF, (ii) nBuLi (4.0 eq) in THF and then addition of MeMgBr (4.6 eq) and ZrCl<sub>4</sub>·(THF)<sub>2</sub> (2.0 eq).

## 2.2. Preparation of Supported Catalyst and Ethylene/1-Hexene Copolymerization

We prepared the supported catalysts using the complexes discussed in the previous sections; the complexes were reacted at 70 °C for 1.0 h with silica–MAO that was beforehand obtained by treatment of silica with methylaluminoxane (MAO) (150 μmol/g-(silica–MAO); Al/Zr = 53), and the resulting supported catalysts were isolated by filtration. In all cases, the filtrates were almost colorless, indicating that most of the metallocene complexes were anchored on the silica–MAO surface. For silica–MAO with optimal MAO coverage (450 mg MAO/g-silica; 4.8 mmol Al/g-(silica–MAO)), we treated silica (~1.0 mmol OH/g; pore volume, 1.6 cm<sup>3</sup>/g; surface area, 309 m<sup>2</sup>/g; pore diameter, 230 nm; mean particle size, 30 μm) with MAO (Me<sub>3</sub>Al content, 13 mol% Al) at a 1:0.5 weight ratio [27,49,50]. We evaluated the performance of each of the prepared supported catalysts via ethylene/1-hexene copolymerization with 6.0 mg of the supported catalysts in hexane (300 mL) containing 1-hexene (3.0 mL) at 80 °C for 30 min under 20 bar ethylene pressure. The supported catalysts prepared with 9–12 containing fluorenyl ligand showed extremely high productivities (21–26 kg PE/g-(supported catalyst)/h; entries 1–4 in Table 1), although 9–12 were used as they contained a slight amount of MgCl<sub>2</sub> impurity. The productivity was higher compared with those of both the supported catalysts prepared using tetramethylcyclopentadienyl analog I (17.5 kg PE/g-(supported catalyst)/h; entry 11) and the conventional (rac-ethylenebis(tetrahydroindenyl))ZrCl<sub>2</sub> ((THI)ZrCl<sub>2</sub>) (12 kg PE/g-(supported catalyst)/h; entry 14). Further, our supported catalysts had productivities comparable to those of the supported catalysts prepared using tetramethylcyclopentadienyl analogs II containing tBuO(CH<sub>2</sub>)<sub>6</sub>-tether and dinuclear complex III (25 and 23 kg PE/g-(supported catalyst)/h; entries 12–13).

One advantage of the supported catalysts of 9–12 containing fluorenyl ligand was that they produced high-molecular-weight polymers ( $M_w$ , 250–330 kDa), with the  $M_w$  values comparable to those of the polymers prepared from the conventional (THI)ZrCl<sub>2</sub> ( $M_w$ , 300 kDa). The supported catalyst prepared with 12 containing 2,7-di(*tert*-butyl)fluorenyl ligand furnished the polymer with the highest molecular weight ( $M_w$ , 334 kDa) and the lowest molecular weight distribution ( $M_w/M_n$ , 2.5, entry 4). Comparatively, the supported catalysts prepared with tetramethylcyclopentadienyl analogs I–III produced polymers with much lower molecular weights ( $M_w$  = 110–125 kDa). The supported catalyst prepared with 13 containing electron-withdrawing chloro-substituents on fluorenyl ligand showed low activity (5.6 kg PE/g-(supported catalyst)/h; entry 3), although a high-molecular-weight polymer was produced ( $M_w$ , 340 kDa; entry 5).

Another advantage of the complexes containing fluorenyl ligand was the higher 1-hexene incorporation capability of 9–12 (1-hexene content, 1.3 mol%) compared to both the tetramethylcyclopentadienyl analogs I–III (0.80 mol%) and (THI)ZrCl<sub>2</sub> (1.0 mol%). A disadvantage of the supported catalysts of 9–12 was the lower bulk density of the generated polymer particles, compared to that of I–III or (THI)ZrCl<sub>2</sub> (0.33–0.36 vs. 0.38 or 0.42 g/mL). The supported catalyst prepared with the 2-methyl-4-(4-*tert*-butylphenyl)indenyl complex 15, for which complete removal of the THF signal was impossible and accordingly contained a substantial amount of MgCl<sub>2</sub> impurity, showed low activity (13.2 kg PE/g-(supported catalyst)/h; entry 6). The supported catalyst prepared with the CGC-type complex 17 showed very low activity (0.75 kg PE/g-(supported catalyst)/h).

**Table 1.** Ethylene/1-hexene copolymerization results for the supported catalysts prepared with *ansa*-zirconocene complexes <sup>a,b</sup>.

Entry	Metallocene Complexes	Productivity (kg – PE/g – (Supported Catalyst)/h)	Bulk Density (g/mL)	1-Hexene Content (mol%)	M <sub>w</sub> <sup>c</sup> (kDa)	M <sub>w</sub> /M <sub>n</sub>
1	<b>9</b> (Me, H, H)	23.0	0.33	1.8	250	2.7
2	<b>10</b> (Me, Me, H)	25.7	0.35	1.3	298	3.6
3	<b>11</b> (H, H, H)	25.8	0.35	1.3	262	5.2
4	<b>12</b> (Me, H, tBu)	20.7	0.36	1.3	334	2.5
5	<b>13</b> (Me, H, Cl)	5.6	0.37	1.1	340	4.1
6	<b>15</b> (tBuPh-indenyl)	13.2	0.35	1.8	246	3.5
7	<b>20</b> (tBuO–, tBu <sub>2</sub> fluorenyl)	19.6	0.35	0.79	373	4.1
8	<b>23</b> (tBuO–, tBuPh-indenyl)	23.2	0.36	1.1	196	5.2
9	<b>26</b> (dinuclear, tBu <sub>2</sub> fluorenyl)	24.5	0.35	1.2	357	4.1
10	<b>I</b> (Me <sub>4</sub> C <sub>5</sub> )	17.5	0.38	0.79	125	3.2
11	<b>II</b> (dinuclear, Me <sub>4</sub> C <sub>5</sub> )	24.8	0.38	0.80	110	3.0
12	<b>III</b> (tBuO, Me <sub>4</sub> C <sub>5</sub> )	22.8	0.38	0.80	114	3.0
13	(THI)ZrCl <sub>2</sub> <sup>d</sup>	12.0	0.42	1.0	300	3.2

<sup>a</sup> Supported catalyst preparation conditions: Silica–MAO (1.0 g, 4.8 mmol Al/g–(silica–MAO)), metallocene complex (120 μmol Zr), 70 °C, 1.0 h. <sup>b</sup> Polymerization conditions: supported catalyst (6.0 mg), hexane (300 mL), 1-hexene (3.0 mL), Et<sub>3</sub>Al (0.20 mmol) as a scavenger, ethylene (20 bar), 80 °C, 30 min. <sup>c</sup> Measured by GPC at 160 °C using trichlorobenzene with PS standards. <sup>d</sup> (rac-ethylenebis(tetrahydroindenyl))ZrCl<sub>2</sub>.

Further, the advantage in terms of activity and molecular weight realized by attaching a tBuO(CH<sub>2</sub>)<sub>6</sub>-tether or constructing a dinuclear congener was marginal in this work (entries 7–9). However, another aspect of the advantage is in the synthesis; dinuclear complex and complexes containing tBuO(CH<sub>2</sub>)<sub>6</sub>-tether are much more soluble in hexane than their mononuclear congeners. This facilitates the isolation of fairly pure complexes, even with containing many chiral centers, via a simple hexane extraction (in high yields and with the complete removal of contaminant THF signals). Complexes **20** and **23** attaching tBuO(CH<sub>2</sub>)<sub>6</sub>-tether and the dinuclear one **26** are not a single compound but a mixture of stereoisomers, and polymers generated with those complexes exhibited rather broad molecular weight distributions (M<sub>w</sub>/M<sub>n</sub>, 4.1, 5.2, and 4.1, respectively), which may be an advantage; polymers with broad molecular weight distributions are usually needed in the polyolefin industry.

### 3. Materials and Methods

#### 3.1. General Remarks

All experiments were performed in an inert atmosphere using a standard glove box and Schlenk techniques. Toluene, hexane, and tetrahydrofuran (THF) were purchased from Thermo Fisher Scientific Korea and distilled from benzophenone ketyl. The hexane (HPLC grade) used for the polymerization reactions was purchased from Thermo Fisher Scientific Korea (Seoul, Korea) and purified over a Na/K alloy. The ethylene gas was purified by contact with molecular sieves and copper for more than 12 h under a pressure of 48 bar. Silica (SYLOPOL-2410) was obtained from GRACE and used as received (Yeosu, South Korea). The <sup>1</sup>H NMR (600 MHz) and <sup>13</sup>C NMR (150 MHz) spectra were recorded on a JEOL (Tokyo, Japan) ECZ 600 instrument. Gel permeation chromatography (GPC) was performed in 1,2,4-trichlorobenzene at 160 °C using an Agilent PL-GPC 220 system equipped with an RI detector and two columns (PLgel mixed-B 7.5 × 300 mm from Varian (Polymer Lab (Salop, UK))).

#### 3.2. Synthesis of **1**

A solution of nBuLi in hexane (8.44 g, 2.5 M, 30.4 mmol) was added dropwise to a solution of thiophene-fused cyclopentadiene compound 2,4,5-Me<sub>3</sub>C<sub>7</sub>H<sub>3</sub>S (5.00 g, 30.4 mmol) in hexane (100 mL) at –78 °C. The resulting solution was slowly warmed to room temperature and then stirred overnight at room temperature to precipitate the corresponding thiophene-fused cyclopentadienyl–Li as a white solid, which was isolated by filtration (4.66 g, 90%).

A solution of  $\text{Me}_2\text{SiCl}_2$  (1.14 g, 8.81 mmol) in toluene (7.0 mL) was added to the prepared Li compound (1.00 g, 5.88 mmol) dispersed in toluene (5.0 mL) at  $-30^\circ\text{C}$ . The solution was slowly warmed to room temperature and stirred overnight at room temperature. After the removal of the solvent using a vacuum line, the product was extracted with hexane (20 mL) via filtration over Celite. The solvent was removed using a vacuum line to obtain the desired compound as a yellowish-brown liquid (1.39 g, 92%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.49 (q,  $^4J = 1.2$  Hz, 1H), 3.23 (s, 1H), 2.28 (s, 3H,  $\text{CH}_3$ ), 1.97 (s, 3H,  $\text{CH}_3$ ), 1.92 (q,  $^4J = 1.2$  Hz, 3H,  $\text{CH}_3$ ), 0.21 (s, 3H,  $\text{SiCH}_3$ ), and 0.02 (s, 3H,  $\text{SiCH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  152.5, 141.6, 136.8, 135.6, 131.0, 116.6, 48.8, 16.0, 14.8, 11.7,  $-0.4$ , and  $-0.8$  ppm. HRMS(EI):  $m/z$  calcd. ( $\text{M}^+$ )  $\text{C}_{12}\text{H}_{17}\text{ClSi}$  256.0509. Found: 256.0509.

### 3.3. Synthesis of 2

Compound 2 was synthesized using the same conditions and procedure as those for 1, with  $(\text{Me}_4\text{C}_7\text{S})^- \text{Li}^+$  (1.08 g, 5.88 mmol). A yellowish-brown liquid compound was obtained in 92% yield (1.46 g).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  3.20 (s, 1H), 2.15 (s, 3H,  $\text{CH}_3$ ), 2.05 (s, 3H,  $\text{CH}_3$ ), 2.00 (s, 3H,  $\text{CH}_3$ ), 1.99 (s, 3H,  $\text{CH}_3$ ), 0.27 (s, 3H,  $\text{SiCH}_3$ ), and 0.03 (s, 3H,  $\text{SiCH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  151.6, 136.8, 134.6, 134.0, 131.8, 125.4, 48.3, 14.6, 13.6, 12.2, 12.1,  $-0.2$ , and  $-0.9$  ppm. HRMS(EI):  $m/z$  calcd. ( $\text{M}^+$ )  $\text{C}_{13}\text{H}_{17}\text{ClSi}$  270.0663. Found: 270.0665.

### 3.4. Synthesis of 3

Compound 3 was synthesized using the same conditions and procedure as those for 1, with  $(\text{Me}_3\text{C}_7\text{H}_2\text{S})^- \text{Li}^+$  (0.92 g, 5.88 mmol). A yellowish-brown liquid compound was obtained in 92% yield (1.31 g).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.00 (d,  $J = 4.8$  Hz, 1H), 6.80 (d,  $J = 4.8$  Hz, 1H), 3.21 (s, 1H), 1.94 (s, 3H,  $\text{CH}_3$ ), 1.89 (s, 3H,  $\text{CH}_3$ ), 0.16 (s, 3H,  $\text{SiCH}_3$ ), and  $-0.01$  (s, 3H,  $\text{SiCH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  152.8, 138.2, 137.7, 130.9, 127.0, 117.8, 48.4, 14.8, 11.7,  $-0.5$ , and  $-0.8$  ppm. HRMS(EI):  $m/z$  calcd. ( $\text{M}^+$ )  $\text{C}_{11}\text{H}_{15}\text{ClSi}$  242.0352. Found: 242.0352.

### 3.5. Synthesis of 4

A solution of nBuLi in hexane (8.34 g, 2.5 M, 30.1 mmol) was added slowly to a solution of fluorene (5.00 g, 30.1 mmol) in toluene (50 mL) at room temperature. The resulting solution was heated to  $80^\circ\text{C}$  and then stirred for 5 h to precipitate fluorenyl-Li as orange solids, which were isolated by filtration (4.66 g, 90%). The prepared fluorenyl-Li (0.248 g, 1.56 mmol) was added to a solution of 1 (0.400 g, 1.56 mmol) in THF (6.0 mL) at  $-30^\circ\text{C}$ , and the mixture was slowly warmed to room temperature. The solution was stirred overnight, and the solvent was removed using a vacuum line. The product was extracted with hexane (20 mL) and collected by filtration over Celite. After removing the solvent using a vacuum line, the product was purified by silica gel column chromatography and eluted with hexane and toluene (30:1,  $v/v$ ). A yellowish-brown, oily compound was obtained (0.181 g, 30%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.80 (d,  $J = 7.6$  Hz, 1H), 7.77 (d,  $J = 7.6$  Hz, 1H), 7.74 (d,  $J = 7.6$  Hz, 1H), 7.34 (d,  $J = 7.6$  Hz, 1H), 7.29 (t,  $J = 7.6$  Hz, 1H), 7.26 (t,  $J = 7.6$  Hz, 1H), 7.24 (t,  $J = 7.6$  Hz, 1H), 7.15 (t,  $J = 7.6$  Hz, 1H), 6.62 (s, 1H), 4.47 (s, 1H), 3.60 (s, 1H), 2.34 (s, 3H,  $\text{CH}_3$ ), 2.00 (s, 3H,  $\text{CH}_3$ ), 1.76 (s, 3H,  $\text{CH}_3$ ),  $-0.28$  (s, 3H,  $\text{SiCH}_3$ ), and  $-0.49$  (s, 3H,  $\text{SiCH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  151.9, 145.5, 141.4, 141.3, 140.7, 138.2, 137.6, 130.1, 126.0, 125.9, 124.7, 124.5, 120.5, 120.4, 116.9, 46.1, 40.8, 16.1, 15.0, 11.9,  $-6.7$ , and  $-7.2$  ppm. HRMS(EI):  $m/z$  calcd. ( $\text{M}^+$ )  $\text{C}_{25}\text{H}_{26}\text{SSi}$  386.1527. Found: 386.1527.

### 3.6. Synthesis of 5

Compound 5 was synthesized under the same conditions and procedure as 4, using 2 (0.423 g, 1.56 mmol). A yellowish-brown, oily compound was obtained by silica gel column chromatography with hexane and toluene (30:1,  $v/v$ ) as eluents (0.269 g, 43%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.79 (d,  $J = 7.6$  Hz, 1H), 7.76 (d,  $J = 7.6$  Hz, 2H), 7.33 (d,  $J = 7.6$  Hz, 1H), 7.29 (t,  $J = 7.6$  Hz, 1H), 7.26 (t,  $J = 7.6$  Hz, 1H), 7.23 (td,  $^3J = 7.6$  Hz,  $^4J = 1.4$  Hz, 1H), 7.13 (td,  $^3J = 7.6$  Hz,  $^4J = 1.4$  Hz, 1H), 4.47 (s, 1H), 3.55 (s, 1H), 2.22 (s, 3H,  $\text{CH}_3$ ), 2.14 (s, 3H,  $\text{CH}_3$ ), 2.07 (s, 3H,  $\text{CH}_3$ ), 1.74 (s, 3H,  $\text{CH}_3$ ),  $-0.23$  (s, 3H,  $\text{SiCH}_3$ ), and  $-0.44$  (s, 3H,  $\text{SiCH}_3$ ) ppm.

ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  151.0, 145.6, 145.6, 141.4, 138.1, 136.0, 133.7, 131.0, 126.7, 126.5, 126.0, 125.8, 125.6, 124.7, 124.6, 120.5, 120.3, 45.6, 40.8, 14.7, 13.7, 12.4, 12.2,  $-6.5$ , and  $-6.9$  ppm. HRMS(EI):  $m/z$  calcd. ((M<sup>+</sup>)  $\text{C}_{26}\text{H}_{28}\text{SSi}$ ) 400.1684. Found: 400.1681.

### 3.7. Synthesis of 6

Compound 6 was synthesized using the same conditions and procedure as those for 4, with 3 (0.379 g, 1.56 mmol). A yellowish-brown, oily compound was obtained by silica gel column chromatography with hexane and toluene (30:1, *v/v*) as eluents (0.174 g, 30%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.78 (d,  $J = 7.6$  Hz, 1H), 7.76 (d,  $J = 7.6$  Hz, 1H), 7.69 (d,  $J = 7.6$  Hz, 1H), 7.30 (d,  $J = 7.6$  Hz, 1H), 7.29 (t,  $J = 7.6$  Hz, 1H), 7.25 (t,  $J = 7.6$  Hz, 1H), 7.23 (td,  $^3J = 7.6$  Hz,  $^4J = 1.4$  Hz, 1H), 7.15 (td,  $^3J = 7.6$  Hz,  $^4J = 1.4$  Hz, 1H), 6.97 (d,  $J = 4.8$  Hz, 1H), 6.86 (d,  $J = 4.8$  Hz, 1H), 4.34 (s, 1H), 3.51 (s, 1H), 1.92 (s, 3H,  $\text{CH}_3$ ), 1.68 (s, 3H,  $\text{CH}_3$ ), and  $-0.39$  (s, 3H,  $\text{SiCH}_3$ ),  $-0.56$  (s, 3H,  $\text{SiCH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  152.3, 145.5, 145.4, 141.4, 141.3, 140.2, 139.2, 130.0, 126.7, 126.5, 126.2, 126.0, 125.9, 124.7, 124.6, 120.5, 120.4, 118.1, 45.7, 40.7, 15.0, 11.8,  $-6.7$ , and  $-7.2$  ppm. HRMS(EI):  $m/z$  calcd. ((M<sup>+</sup>)  $\text{C}_{24}\text{H}_{24}\text{SSi}$ ) 372.1368. Found: 372.1371.

### 3.8. Synthesis of 7

A solution of *n*BuLi in hexane (4.98 g, 2.5 M, 18.0 mmol) was added dropwise to a solution of 2,7-di-*tert*-butylfluorene (5.00 g, 18.0 mmol) in toluene (50 mL) at room temperature. The resulting solution was heated to 80 °C and then stirred for 5 h to precipitate 2,7-di-*tert*-butylfluorenyl-Li as a yellow solid, which was isolated by filtration (4.32 g, 85%). Compound 7 was prepared using the same conditions and procedures as those for 4, with the prepared 2,7-di-*tert*-butylfluorenyl-Li (0.444 g, 1.56 mmol). A yellowish-brown oily compound was obtained via silica gel column chromatography with hexane and toluene (30:1, *v/v*) as eluents (0.210 g, 27%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  8.02 (s, 1H), 7.83 (d,  $J = 8.3$  Hz, 1H), 7.80 (d,  $J = 8.3$  Hz, 1H), 7.54 (s, 1H), 7.43 (dd,  $^3J = 8.3$  Hz,  $^4J = 1.4$  Hz, 1H), 7.34 (dd,  $^3J = 8.3$  Hz,  $^4J = 1.4$  Hz, 1H), 6.64 (q,  $J = 1.2$  Hz, 1H), 4.47 (s, 1H), 3.74 (s, 1H), 2.35 (s, 3H,  $\text{CH}_3$ ), 2.02 (s, 3H,  $\text{CH}_3$ ), 1.86 (s, 3H,  $\text{CH}_3$ ), 1.39 (s, 9H, *t*Bu), 1.32 (s, 9H, *t*Bu),  $-0.15$  (s, 3H,  $\text{SiCH}_3$ ), and  $-0.40$  (s, 3H,  $\text{SiCH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  152.0, 149.3, 149.1, 145.8, 145.7, 140.8, 139.1, 139.0, 138.2, 137.7, 130.2, 123.2, 123.1, 124.9, 121.6, 121.5, 119.9, 119.8, 117.0, 46.4, 40.6, 35.1, 34.9, 31.9, 31.9, 16.1, 15.1, 11.9,  $-6.3$ , and  $-6.9$  ppm. HRMS(EI):  $m/z$  calcd. ((M<sup>+</sup>)  $\text{C}_{33}\text{H}_{42}\text{SSi}$ ) 498.2774. Found: 498.2776. The yield was improved by reversing the reaction sequence. Thus, *tert*-butyl methyl ether (0.889 g, 3.3 eq/Li<sup>+</sup>) was added to a solution of 2,7-di(*tert*-butyl)fluorenyl-Li (0.766 g, 2.70 mmol) in hexane (27 mL) *tert*-butyl methyl ether (0.889 g, 3.3 eq/Li<sup>+</sup>). After cooling to  $-78$  °C, a solution of  $\text{Me}_2\text{SiCl}_2$  (0.522 g, 4.04 mmol) in hexane (7.5 mL) was added. After overnight stirring at room temperature, the solvent was removed under vacuum. The product was extracted using hexane (15 mL). The extract was collected by filtration over Celite. The solvent was removed using a vacuum line to obtain 2,7-di(*tert*-butyl)fluorenyl-Si(Me)Cl (0.90 g, 90%). The prepared 2,7-di(*tert*-butyl)fluorenyl-Si(Me)Cl was dissolved in THF (10 mL). After cooling to  $-30$  °C, thiophene-fused cyclopentadienyl-Li compound (2,4,5- $\text{Me}_3\text{C}_7\text{H}_2\text{S}$ )Li (0.413 g, 2.43 mmol) was added. The solution was stirred overnight, and the solvent was removed using a vacuum line. The product was extracted with hexane (15 mL) and collected by filtration over Celite. After removing the solvent using a vacuum line, the product was purified by silica gel column chromatography with hexane and toluene (30:1, *v/v*) as eluents. A yellowish-brown, oily compound was obtained in 81% yield (0.98 g).

### 3.9. Synthesis of 8

A solution of *n*BuLi in hexane (5.90 g, 2.5 M, 21.3 mmol) was added dropwise to a solution of 2,7-dichlorofluorene (5.00 g, 21.3 mmol) in toluene (50 mL) at  $-78$  °C. The resulting solution was stirred overnight to precipitate 2,7-dichlorofluorenyl-Li as a light-yellow solid, which was isolated by filtration (4.51 g, 88%). Compound 8 was prepared using the same conditions and procedures as those for 4, with the prepared 2,7-dichlorofluorenyl-Li

(0.376 g, 1.56 mmol). A yellowish-brown, oily compound was obtained by silica gel column chromatography with hexane and toluene (30:1, *v/v*) as eluents (0.412 g, 58%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.58 (s, 1H), 7.28 (d,  $J = 8.3$  Hz, 1H), 7.25 (s, 1H), 7.24 (d,  $J = 8.3$  Hz, 1H), 7.22 (dd,  $^3J = 8.3$  Hz,  $^4J = 1.4$  Hz, 1H), 7.17 (dd,  $^3J = 8.3$  Hz,  $^4J = 1.4$  Hz, 1H), 6.52 (s, 1H), 3.91 (s, 1H), 3.21 (s, 1H), 2.37 (s, 3H,  $\text{CH}_3$ ), 1.92 (s, 3H,  $\text{CH}_3$ ), 1.62 (s, 3H,  $\text{CH}_3$ ),  $-0.33$  (s, 3H,  $\text{SiCH}_3$ ), and  $-0.36$  (s, 3H,  $\text{SiCH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  151.9, 147.3, 147.1, 141.0, 138.7, 138.5, 137.8, 137.1, 132.6, 132.5, 130.4, 126.4, 126.2, 124.9, 124.9, 121.2, 121.1, 117.0, 45.9, 40.9, 16.1, 14.7, 11.8,  $-5.4$ , and  $-5.9$  ppm. HRMS(EI): *m/z* calcd. (( $\text{M}^+$ )  $\text{C}_{25}\text{H}_{24}\text{Cl}_2\text{SSi}$ ) 454.0741. Found: 454.0745.

### 3.10. Synthesis of **9**

A solution of *n*BuLi in hexane (1.11 g, 2.5 M, 4.02 mmol) was added dropwise to a solution of **4** (0.777 g, 2.01 mmol) in THF (3.5 mL) at  $-30$  °C. After slowly warming to room temperature, the solution was stirred at room temperature for 1 h. After cooling to  $-30$  °C again, MeMgBr (1.41 mL, 1.37 M solution in THF–toluene, 4.62 mmol) and  $\text{ZrCl}_4 \cdot (\text{THF})_2$  (0.743 g, 1.97 mmol) were added successively. After the solution was stirred overnight at room temperature, the solvent was removed using a vacuum line. The product was extracted with toluene (30 mL) and collected by filtration over Celite. The solvent was removed using a vacuum line to obtain a yellowish-brown solid, which was redissolved in toluene (4 mL). Yellow solids were deposited when the solution was stored in a freezer at  $-30$  °C (0.906 g, 91%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.95 (d,  $J = 8.3$  Hz, 1H), 7.85 (d,  $J = 8.3$  Hz, 1H), 7.73 (d,  $J = 8.3$  Hz, 1H), 7.45 (d,  $J = 8.3$  Hz, 1H), 7.34 (t,  $J = 8.3$  Hz, 1H), 7.24 (t,  $J = 8.3$  Hz, 1H), 7.00 (t,  $J = 8.3$  Hz, 2H), 6.17 (q,  $^4J = 1.2$  Hz, 1H), 2.07 (q,  $J = 1.2$  Hz, 3H,  $\text{CH}_3$ ), 2.00 (s, 3H,  $\text{CH}_3$ ), 1.75 (s, 3H,  $\text{CH}_3$ ), 1.06 (s, 3H,  $\text{SiCH}_3$ ), 0.83 (s, 3H,  $\text{SiCH}_3$ ),  $-1.08$  (s, 3H,  $\text{ZrCH}_3$ ), and  $-1.57$  (s, 3H,  $\text{ZrCH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  145.2, 140.1, 132.4, 131.0, 129.1, 128.7, 127.4, 126.9, 126.7, 126.4, 126.1, 125.4, 124.8, 124.0, 123.5, 123.4, 117.1, 116.0, 77.0, 62.7, 40.8, 38.3, 16.2, 15.5, 12.2, 1.5, and 1.3 ppm.

### 3.11. Synthesis of **10**

Compound **10** was synthesized using the same conditions and procedure as those for **9**, with **5** (0.175 g, 0.437 mmol). A yellow solid was obtained in 73% yield (0.166 g).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.95 (d,  $J = 8.3$  Hz, 1H), 7.85 (d,  $J = 8.3$  Hz, 1H), 7.74 (d,  $J = 8.3$  Hz, 1H), 7.45 (d,  $J = 8.3$  Hz, 1H), 7.34 (t,  $J = 8.3$  Hz, 1H), 7.23 (t,  $J = 8.3$  Hz, 1H), 7.01 (td,  $^3J = 8.3$  Hz,  $^4J = 1.4$  Hz, 1H), 7.00 (td,  $^3J = 8.3$  Hz,  $^4J = 1.4$  Hz, 1H), 2.06 (s, 3H,  $\text{CH}_3$ ), 1.96 (s, 3H,  $\text{CH}_3$ ), 1.87 (s, 3H,  $\text{CH}_3$ ), 1.76 (s, 3H,  $\text{CH}_3$ ), 1.08 (s, 3H,  $\text{SiCH}_3$ ), 0.84 (s, 3H,  $\text{SiCH}_3$ ),  $-1.08$  (s, 3H,  $\text{ZrCH}_3$ ), and  $-1.60$  (s, 3H,  $\text{ZrCH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  140.1, 137.1, 132.6, 131.1, 129.5, 127.7, 127.3, 126.8, 126.7, 126.6, 126.5, 125.4, 124.8, 124.4, 123.9, 123.4, 123.4, 117.6, 76.7, 62.8, 39.7, 38.5, 15.3, 13.5, 12.4, 11.9, 1.7, and 1.2 ppm.

### 3.12. Synthesis of **11**

Compound **11** was synthesized using the same conditions and procedure as those for **9**, with **6** (0.233 g, 0.626 mmol). A yellow solid was obtained in 60% yield (0.181 g).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.92 (d,  $J = 8.3$  Hz, 1H), 7.83 (d,  $J = 8.3$  Hz, 1H), 7.70 (d,  $J = 8.3$  Hz, 1H), 7.45 (d,  $J = 8.3$  Hz, 1H), 7.34 (t,  $J = 8.3$  Hz, 1H), 7.23 (t,  $J = 8.3$  Hz, 1H), 7.00 (td,  $^3J = 8.3$  Hz,  $^4J = 1.4$  Hz, 1H), 6.99 (td,  $^3J = 8.3$  Hz,  $^4J = 1.4$  Hz, 1H), 6.73 (d,  $J = 5.4$  Hz, 1H), 6.44 (d,  $J = 5.4$  Hz, 1H), 1.97 (s, 3H,  $\text{CH}_3$ ), 1.74 (s, 3H,  $\text{CH}_3$ ), 1.04 (s, 3H,  $\text{SiCH}_3$ ), 0.82 (s, 3H,  $\text{SiCH}_3$ ),  $-1.10$  (s, 3H,  $\text{ZrCH}_3$ ), and  $-1.65$  (s, 3H,  $\text{ZrCH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  139.5, 132.4, 131.2, 130.5, 129.9, 129.4, 129.3, 127.4, 126.8, 126.6, 126.2, 125.4, 124.8, 124.0, 123.5, 123.5, 118.3, 117.5, 76.9, 62.9, 41.9, 38.6, 15.5, 12.1, 1.6, and 1.3 ppm.

### 3.13. Synthesis of **12**

Compound **12** was synthesized using the same conditions and procedure as those for **9**, with **7** (0.295 g, 0.591 mmol). A yellow solid was obtained in 24% yield (0.086 g). The solubility of this compound in  $\text{C}_6\text{D}_6$  was too low to record the  $^{13}\text{C}$  NMR spectrum.

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.96, (d,  $J = 8.3$  Hz, 1H), 7.87 (d,  $J = 8.3$  Hz, 1H), 7.76 (s, 1H), 7.58 (s, 1H), 7.50 (dd,  $^3J = 8.3$  Hz,  $^4J = 1.4$  Hz, 1H), 7.43 (dd,  $^3J = 8.3$  Hz,  $^4J = 1.4$  Hz, 1H), 6.22 (q,  $^4J = 1.2$  Hz, 1H), 2.12 (q,  $^4J = 1.2$  Hz, 3H,  $\text{CH}_3$ ), 2.03 (s, 3H,  $\text{CH}_3$ ), 1.87 (s, 3H,  $\text{CH}_3$ ), 1.35 (s, 9H, tBu), 1.30 (s, 9H, tBu), 1.16 (s, 3H,  $\text{SiCH}_3$ ), 0.98 (s, 3H,  $\text{SiCH}_3$ ),  $-1.09$  (s, 3H,  $\text{ZrCH}_3$ ), and  $-1.59$  (s, 3H,  $\text{ZrCH}_3$ ) ppm.

### 3.14. Synthesis of 13

Compound **13** was synthesized using the same conditions and procedure as those for **9**, with **8** (0.200 g, 0.440 mmol). A yellow solid was obtained in 74% yield (0.183 g).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.75 (s, 1H), 7.53 (s, 1H), 7.52 (d,  $J = 8.3$  Hz, 1H), 7.41 (d,  $J = 8.3$  Hz, 1H), 7.31 (dd,  $^3J = 8.3$  Hz,  $^4J = 1.4$  Hz, 1H), 7.21 (dd,  $^3J = 8.3$  Hz,  $^4J = 1.4$  Hz, 1H), 6.09 (q,  $^4J = 1.2$  Hz, 1H), 2.05 (q,  $^4J = 1.2$  Hz, 3H,  $\text{CH}_3$ ), 1.93 (s, 3H,  $\text{CH}_3$ ), 1.72 (s, 3H,  $\text{CH}_3$ ), 0.89 (s, 3H,  $\text{SiCH}_3$ ), 0.67 (s, 3H,  $\text{SiCH}_3$ ),  $-1.06$  (s, 3H,  $\text{ZrCH}_3$ ), and  $-1.56$  (s, 3H,  $\text{ZrCH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  125.9, 140.3, 133.2, 133.0, 133.0, 131.8, 129.7, 129.3, 126.5, 125.8, 125.0, 124.3, 124.2, 124.1, 123.6, 123.2, 117.7, 115.8, 77.2, 63.7, 41.4, 38.8, 16.1, 15.3, 12.1, 0.9, and 0.8 ppm.

### 3.15. Synthesis of 14

A solution of *n*BuLi in hexane (3.17 g, 2.5 M, 1.14 mmol) was added dropwise to a solution of 2-methyl-4-(4-*tert*-butylphenyl)indenene (3.00 g, 1.14 mmol) in hexane (30 mL), and the resulting solution was stirred overnight. A light-yellow solid precipitated was isolated by filtration (2.54 g, 83%). Compound **14** was synthesized using the same conditions and procedures as those for **4**, with the prepared 2-methyl-4-(4-*tert*-butylphenyl)indenyl-Li (0.420 g, 1.56 mmol). A yellowish-brown, oily compound was obtained by silica gel column chromatography with hexane and toluene (30:1, *v/v*) as eluents (0.445 g, 59%). The product was obtained as a mixture of two diastereomers in a ratio of 1.0:0.10. Signals for minor isomers were not recorded (see Figure S14).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.64 (d,  $J = 8.3$  Hz, 2H), 7.42 (d,  $J = 7.6$  Hz, 1H), 7.41 (d,  $J = 8.3$  Hz, 2H), 7.28 (d,  $J = 7.6$  Hz, 1H), 7.14 (t,  $J = 7.6$  Hz, 1H), 7.00 (s, 1H), 6.62 (s, 1H), 6.96 (s, 1H), 6.62 (s, 1H), 3.99 (s, 1H), 3.49 (s, 1H), 2.33 (s, 3H,  $\text{CH}_3$ ), 2.14 (s, 3H,  $\text{CH}_3$ ), 2.02 (s, 3H,  $\text{CH}_3$ ), 1.89 (s, 3H,  $\text{CH}_3$ ), 1.31 (s, 9H, tBu),  $-0.19$  (s, 3H,  $\text{SiCH}_3$ ), and  $-0.26$  (s, 3H,  $\text{SiCH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  152.1, 149.7, 147.5, 146.1, 143.7, 140.7, 139.3, 138.3, 137.7, 134.7, 130.2, 129.2, 126.7, 126.0, 125.7, 123.6, 122.5, 116.8, 47.6, 46.4, 34.6, 31.6, 18.0, 16.0, 15.1, 11.8,  $-6.3$ , and  $-6.8$  ppm.

### 3.16. Synthesis of 15

Compound **15** was synthesized using the same conditions and procedure as those for **9**, with **14** (0.207 g, 0.428 mmol). A yellow solid was obtained in 67% yield (0.178 g), as a mixture of two isomers in a 1.0:0.54 ratio (refer to Figure S15a), which was used for polymerization without separation of the isomers. Solids (0.074 g) were deposited in a toluene solution containing 0.250 g of the isomer mixture and were stored in a freezer at  $-30$  °C. The  $^1\text{H}$  NMR spectrum of the deposited solids indicated that, mainly, the minor isomer in the crude mixture was deposited, along with a small portion of the major isomer, in a 1.0:0.13 ratio (refer to Figure S15b). Contaminant THF signals (0.5 eq) were detected even after crystallization.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) of major isomer:  $\delta$  7.88 (d,  $J = 8.3$  Hz, 2H), 7.64 (d,  $J = 8.3$  Hz, 1H), 7.41 (d,  $J = 8.3$  Hz, 2H), 7.25 (d,  $J = 8.3$  Hz, 1H), 7.24 (s, 1H), 6.87 (dd,  $J = 9.0$  Hz and 6.9 Hz, 1H), 6.26 (s, 1H), 2.14 (s, 3H,  $\text{CH}_3$ ), 2.09 (s, 3H,  $\text{CH}_3$ ), 1.98 (s, 3H,  $\text{CH}_3$ ), 1.83 (s, 3H,  $\text{CH}_3$ ), 1.25 (s, 9H, tBu), 1.00 (s, 3H,  $\text{SiCH}_3$ ), 0.65 (s, 3H,  $\text{SiCH}_3$ ), 0.12 (s, 3H,  $\text{ZrCH}_3$ ), and  $-1.38$  (s, 3H,  $\text{ZrCH}_3$ ) ppm.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) of minor isomer:  $\delta$  7.85 (d,  $J = 8.3$  Hz, 2H), 7.36 (d,  $J = 8.3$  Hz, 1H), 7.35 (d,  $J = 8.3$  Hz, 2H), 7.25 (d,  $J = 8.3$  Hz, 1H), 7.24 (s, 1H), 6.90 (dd,  $J = 9.0$  Hz and 6.9 Hz, 1H), 6.38 (s, 1H), 2.20 (s, 3H,  $\text{CH}_3$ ), 2.19 (s, 3H,  $\text{CH}_3$ ), 2.06 (s, 3H,  $\text{CH}_3$ ), 1.76 (s, 3H,  $\text{CH}_3$ ), 1.24 (s, 9H, tBu), 0.80 (s, 3H,  $\text{SiCH}_3$ ), 0.77 (s, 3H,  $\text{SiCH}_3$ ),  $-0.43$  (s, 3H,  $\text{ZrCH}_3$ ), and  $-0.91$  (s, 3H,  $\text{ZrCH}_3$ ) ppm.

### 3.17. Synthesis of **16**

Compound **16** was synthesized using the same conditions and procedures as those for **4**, with *tert*-BuN(H)Li (0.126 g, 1.59 mmol). A yellowish-brown liquid was obtained (0.423 g, 91%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.61 (q,  $^4J = 1.2$  Hz, 1H), 3.22 (s, 1H), 2.36 (s, 3H, CH<sub>3</sub>), 2.04 (s, 3H, CH<sub>3</sub>), 2.04 (s, 3H, CH<sub>3</sub>), 1.12 (s, 9H, tBu), 0.63 (s, 1H, NH), 0.12 (s, 3H, SiCH<sub>3</sub>), and  $-0.03$  (s, 3H, SiCH<sub>3</sub>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  151.3, 139.7, 138.3, 138.1, 129.0, 116.5, 50.3, 49.6, 33.9, 16.1, 15.2, 11.9, 0.0, and  $-1.6$  ppm. HRMS(EI):  $m/z$  calcd. ((M<sup>+</sup>) C<sub>16</sub>H<sub>27</sub>NSSi) 293.1633. Found: 293.1631.

### 3.18. Synthesis of **17**

A measured quantity of nBuLi (0.60 mL, 2.5 M in hexane, 1.51 mmol) was added dropwise at  $-78$  °C to **16** (0.221 g, 0.754 mmol) dissolved in THF (2.0 g). After stirring overnight at room temperature, the solution was cooled to  $-78$  °C. Subsequently, MeMgCl (0.52 mL, 3.1 M in THF, 1.58 mmol) and TiCl<sub>4</sub>·DME (0.211 g, 0.739 mmol) were added. The resulting solution was stirred overnight at room temperature. After the volatiles were removed using a vacuum line, the product was extracted with hexane (13 mL). The extract was collected by filtration over Celite. The solvent was removed using a vacuum line to obtain a yellowish-brown solid (0.133 g, 47%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.39 (q,  $^4J = 1.8$  Hz, 1H), 2.20 (s, 3H, CH<sub>3</sub>), 2.19 (q,  $^4J = 1.8$  Hz, 3H, CH<sub>3</sub>), 1.89 (s, 3H, CH<sub>3</sub>), 1.53 (s, 9H, tBu), 0.66 (s, 3H, CH<sub>3</sub>), 0.56 (s, 3H, CH<sub>3</sub>), 0.46 (s, 3H, CH<sub>3</sub>), and 0.25 (s, 3H, CH<sub>3</sub>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  147.2, 141.4, 137.2, 136.8, 122.1, 116.4, 88.2, 57.9, 55.8, 52.8, 34.7, 16.4, 15.6, 12.6, 4.6, and 4.2 ppm.

### 3.19. Synthesis of **18**

A measured amount of *tert*-butyl methyl ether (0.886 g, 3 eq/Li<sup>+</sup>) was added to a solution of 2,7-di-*tert*-butylfluorenyl-Li (0.853 g, 3.00 mmol) in hexane (30 mL). After cooling to  $-78$  °C, a solution of tBuO(CH<sub>2</sub>)<sub>6</sub>(Me)SiCl<sub>2</sub> (0.814 g, 3.00 mmol) in hexane (7.5 mL) was added. After stirring overnight at room temperature, the solvent was removed under vacuum. The product was extracted using hexane (15 mL). The extract was collected by filtration over Celite. The solvent was removed using a vacuum line to obtain the desired compound (1.51 g, 98%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.89 (s, 1H), 7.81 (s, 1H), 7.77 (s, 1H), 7.76 (s, 1H), 7.42 (t,  $J = 2.07$  Hz, 1H), 7.41 (t,  $J = 2.07$  Hz, 1H), 1.50 (m, 2H), 1.39 and 1.37 (s, 18H, tBu), 1.27–1.02 (m, 6H), 1.13 (s, 9H, OtBu) 0.62–0.42 (m, 2H), and 0.09 (s, 3H, SiCH<sub>3</sub>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  149.4, 143.5, 139.0, 123.8, 122.3, 119.8, 72.0, 61.5, 43.1, 35.0, 33.2, 31.9, 30.9, 27.8, 26.3, 23.2, 15.7, and  $-1.5$  ppm. HRMS(EI):  $m/z$  calcd. ((M<sup>+</sup>) C<sub>32</sub>H<sub>49</sub>CIOSi) 512.3240. Found: 512.3241.

### 3.20. Synthesis of **19**

Thiophene-fused cyclopentadiene 2,4,5-Me<sub>3</sub>C<sub>7</sub>H<sub>3</sub>S (0.325 g, 2.00 mmol) in THF (2.0 mL) was added to a Schlenk flask containing KH (0.104 g, 2.6 mmol) and THF (2.0 mL). After stirring overnight at room temperature, the solution was filtered over Celite to remove the remaining KH, owing to its addition in excess. To the filtrate were added CuCN (1.8 mg, 1 mol%) and a solution of **18** (1.02 g, 2.00 mmol) in THF (15 mL) cooled at  $-30$  °C. The solution was stirred overnight, and the solvent was removed using a vacuum line. The product was extracted with hexane (30 mL) and collected by filtration over Celite. After removing the solvent using a vacuum line, the product was purified by silica gel column chromatography with hexane and diethyl ether (30:1, *v/v*) as eluents. A yellowish-brown, oily compound was obtained (0.854 g, 67%). The  $^1\text{H NMR}$  spectrum of the product was too complicated for complete analysis because of the mixture of the four diastereomers (Figure S19). HRMS(EI):  $m/z$  calcd. ((M<sup>+</sup>) C<sub>42</sub>H<sub>60</sub>OSSi) 640.4138. Found: 640.4134.

### 3.21. Synthesis of **20**

A solution of nBuLi in hexane (0.300 g, 2.5 M, 1.08 mmol) was added dropwise to a solution of **19** (0.347 g, 0.541 mmol) in THF (2 mL) at  $-30$  °C, and the mixture was slowly

warmed to room temperature. After the solution was stirred for 1 h at room temperature, the solution was cooled to  $-30\text{ }^{\circ}\text{C}$ . MeMgBr (0.91 mL, 1.37 M solution in THF-toluene, 1.24 mmol). Next,  $\text{ZrCl}_4\cdot(\text{THF})_2$  (0.200 g, 0.530 mmol) were successively added, and the solution was slowly warmed to room temperature. After stirring overnight, the solvent was removed under vacuum. The product was extracted with hexane (25 mL) and collected by filtration over Celite. The solvent was removed using a vacuum line to obtain a yellow solid (0.379 g, 94%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.97 and 7.95 (d,  $J = 1.4$  Hz, 1H), 7.87 (d,  $J = 8.3$  Hz, 1H), 7.79 and 7.78 (s, 1H), 7.64 and 7.62 (s, 1H), 7.51 and 7.50 (dd,  $^3J = 3.4$  Hz,  $^4J = 1.4$  Hz, 1H), 7.44 and 7.42 (dd,  $^3J = 8.7$  Hz,  $^4J = 1.4$  Hz, 1H), 6.23 (q,  $^4J = 1.4$  Hz, 1H), 3.31 and 3.30 (q,  $J = 6.2$  Hz, 2H), 2.13 (d,  $^4J = 1.4$  Hz, 3H,  $\text{SCCH}_3$ ), 2.03 (s, 3H,  $\text{CH}_3$ ), 1.93 and 1.89 (s, 3H,  $\text{CH}_3$ ), 1.39, 1.36, 1.34, and 1.32 (s, 18H, tBu), 1.26 and 1.08 (s, 3H,  $\text{Si-CH}_3$ ), 1.15 and 1.14 (s, 9H, OtBu),  $-1.07$  and  $-1.08$  (s, 3H,  $\text{ZrCH}_3$ ), and  $-1.58$  (s, 3H,  $\text{ZrCH}_3$ ) ppm. Anal. Calcd. ( $\text{C}_{44}\text{H}_{64}\text{OSSiZr}$ ): C, 69.5; H, 8.48; and S, 4.31%. Found: C, 68.2; H, 8.04; and S, 4.08%.

### 3.22. Synthesis of 21

Compound **21** was synthesized using the same conditions and procedure as those for **18**, with 2-methyl-4-(4-*tert*-butylphenyl)indenyl-Li (0.805 g, 3.00 mmol). A yellow oily compound was obtained in 98% yield (1.46 g).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.58 (d,  $J = 2.1$  Hz, 1H), 7.56 (d,  $J = 2.1$  Hz, 1H), 7.50 and 7.42 (d,  $J = 7.6$  Hz, 1H), 7.41 (d,  $J = 2.1$  Hz, 1H), 7.40 (d,  $J = 2.1$  Hz, 1H), 7.19 and 7.16 (t,  $J = 7.6$  Hz, 1H), 6.89 (s, 1H), 3.47 and 3.44 (s, 1H), 3.26 and 3.21 (t,  $J = 6.2$  Hz, 2H,  $\text{OCH}_2$ ), 2.12 and 2.10 (s, 3H,  $\text{CH}_3$ ), 1.57–1.47 (m, 2H,  $\text{CH}_2$ ), 1.40–1.20 (m, 6H,  $\text{CH}_2$ ), 1.30 (s, 9H, tBu), 1.15 and 1.12 (s, 9H, OtBu), 0.84–0.39 (m, 2H,  $\text{CH}_2$ ), 0.28 and 0.02 (s, 3H,  $\text{SiCH}_3$ ) ppm. HRMS(EI):  $m/z$  calcd. ((M+)  $\text{C}_{31}\text{H}_{45}\text{ClOSi}$ ) 496.2930. Found: 496.2928.

### 3.23. Synthesis of 22

Compound **22** was synthesized using the same conditions and procedure as those for **19**, with **21** (0.955 g, 2.00 mmol). A yellowish-brown oil was obtained in 90% yield (1.11 g). The  $^1\text{H NMR}$  spectrum of the product was too complicated for complete analysis because of the mixture of four diastereomers (Figure S21). HRMS(EI):  $m/z$  calcd. ((M+)  $\text{C}_{41}\text{H}_{56}\text{OSSi}$ ) 624.3818. Found: 624.3821.

### 3.24. Synthesis of 23

Compound **23** was synthesized using the same conditions and procedure as those for **20**, with **22** (0.396 g, 0.633 mmol). A yellow oil was obtained in 92% yield (0.427 g). It was isolated as a mixture of four diastereomers owing to the presence of three chiral centers. Signals of racemic-type and meso-type complexes in a 1.0:0.40 (or vice versa) ratio were further split into 1:0.9 and 1:1 ratios, respectively, due to the chiral center on the Si atom. Signals assigned to minor meso-type complexes are indicated in italics.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.90–7.87 and 7.86–7.84 (m, 2H, 4-*t*BuPh-H), 7.73, 7.70, 7.39, and 7.37 (d,  $J = 8.7$  Hz, 1H), 7.49, 7.42, 7.29, and 7.27 (d,  $J = 8.3$  Hz, 1H), 7.42–7.38 (m, 2H, 4-*t*BuPh-H), 7.31 and 7.29 (s, 1H, indenyl-H), 6.96–6.89 (m, 1H), 6.37 and 6.25 (m, 1H, thiophene-H), 3.33–3.29 (m, 2H,  $\text{OCH}_2$ ), 2.26, 2.24, 2.15, and 2.14 (s, 3 H,  $\text{CH}_3$ ), 2.19, 2.18, 2.09, and 2.08 (d,  $^4J = 1.4$  Hz, 3H,  $\text{SCCH}_3$ ), 2.07, 2.03, and 2.00 (s, 3H,  $\text{CH}_3$ ), 1.88, 1.86, 1.84, and 1.78 (s, 3 H, indenyl- $\text{CH}_3$ ), 1.75–1.25 (m, 10H,  $\text{CH}_2$ ), 1.24, 1.23, and 1.23 (s, 9H, tBu), 1.16, 1.16, 1.16, and 1.15 (s, 9H, tBu), 1.08, 0.89, 0.84, and 0.73 (s, 3H,  $\text{SiCH}_3$ ), 0.18 and  $-0.37$  (s, 3H,  $\text{Zr-CH}_3$ ),  $-0.84$ ,  $-0.85$ ,  $-1.31$ , and  $-1.32$  (s, 3H,  $\text{Zr-CH}_3$ ). Anal. Calcd. ( $\text{C}_{43}\text{H}_{60}\text{OSSiZr}$ ): C, 69.4; H, 8.13; S, 4.31%. Found: C, 68.2; H, 7.77; and S, 4.47%.

### 3.25. Synthesis of 24

A measured amount of *tert*-butyl methyl ether (0.716 g, 3.3 eq/ $\text{Li}^+$ ) was added to a suspension of 2,7-di-*tert*-butylfluorenyl-Li (0.700 g, 2.46 mmol) in hexane (15 mL). After cooling to  $-78\text{ }^{\circ}\text{C}$ , a solution of  $\text{Cl}_2\text{Si}(\text{Me})\text{-(CH}_2)_6\text{-(Me)SiCl}_2$  (0.384 g, 1.23 mmol) in hexane (5 mL) was added. After stirring overnight at room temperature, the solvent was removed

under vacuum. The product was extracted using hexane (15 mL). The extract was collected by filtration over the Celite. The solvent was removed using a vacuum line to obtain a white solid (0.97 g, 99%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.88 (s, 2H), 7.79 (s, 2H), 7.77 (s, 2H), 7.76 (s, 2H), 7.42 (t,  $J = 2.07$  Hz, 2H), 7.41 (t,  $J = 2.07$  Hz, 2H), 4.01 (s, 2H), 1.39 and 1.37 (s, 36H, tBu), 1.08–0.91 (m, 4H), 0.85–0.80 (m, 4H), 0.51–0.32 (m, 4H), and 0.11 (s, 6H,  $\text{SiCH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  149.4, 143.4, 138.9, 123.8, 122.2, 119.8, 43.1, 35.1, 32.7, 31.9, 23.0, 15.5, and  $-1.4$  ppm.

### 3.26. Synthesis of 25

Thiophene-fused cyclopentadiene 2,4,5- $\text{Me}_3\text{C}_7\text{H}_3\text{S}$  (0.284 g, 1.7 mmol) in THF (2.0 mL) was added to a Schlenk flask containing KH (0.090 g, 2.2 mmol) and THF (2.0 mL). After stirring overnight at room temperature, the solution was filtered over Celite to remove the remaining KH, because of its addition in excess. To the filtrate were added CuCN (0.8 mg, 1 mol%) and a solution of **24** (0.69 g, 0.87 mmol) in THF (7 mL) cooled at  $-30$  °C. The solution was stirred overnight, and the solvent was removed using a vacuum line. The product was extracted with hexane (20 mL) and collected by filtration over Celite. A yellowish-brown, oily compound was obtained (0.818 g, 90%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.95 (m, 2H), 7.82 (m, 4H), 7.57 (m, 2H), 7.41 (m, 4H), 6.62 (m, 2H), 4.34 (m, 2H), 3.72 (m, 2H), 2.35 (m, 6H), 2.35 (m, 6H), 2.03 (s, 6H), 1.95 (m, 6H), 1.38 (m, 36H, tBu), 1.27 (m, 6H), 0.50 (m, 6H),  $-0.05$  (m, 3H,  $\text{SiCH}_3$ ), and  $-0.27$  (m, 3H,  $\text{SiCH}_3$ ) ppm.

### 3.27. Synthesis of 26

A solution of nBuLi in hexane (0.621 g, 2.5 M, 2.28 mmol) was added dropwise to a solution of **25** (0.600 g, 0.570 mmol) in THF (6 mL) at  $-30$  °C, and the mixture was slowly warmed to room temperature. After the solution was stirred for 1 h at room temperature, the solution was cooled to  $-30$  °C. MeMgBr (1.92 mL, 1.37 M solution in THF–toluene, 2.62 mmol) and  $\text{ZrCl}_4 \cdot (\text{THF})_2$  (0.421 g, 1.12 mmol) were successively added, and the solution was slowly warmed to room temperature. After stirring overnight, the solvent was removed under vacuum. The product was extracted with hexane (30 mL) and collected by filtration over Celite. The solvent was removed using a vacuum line to obtain a yellow oily compound (0.456 g, 62%).  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.95 (m, 2H), 7.86 (m, 2H), 7.79 (m, 2H), 7.64 (m, 2H), 7.50 (m, 2H), 7.42 (m, 2H), 6.23 (m, 2H), 2.13 (m, 6H), 2.03 (m, 6H), 1.92 (s, 6H), 1.35 (m, 36H, tBu), 1.27 (m, 3H,  $\text{SiCH}_3$ ), 1.10 (m, 3H,  $\text{SiCH}_3$ ), 1.65 (m, 6H), 1.25 (m, 6H),  $-1.08$  (m, 3H,  $\text{ZrCH}_3$ ), and  $-1.58$  (m, 3H,  $\text{ZrCH}_3$ ) ppm.

### 3.28. Preparation of Supported Catalysts

Methylaluminoxane (MAO, 5.0 g, GRACE, 10 wt.% in toluene) was added to a solution of silica (GRACE, SYLOPOL-2410, 1.0 g) in toluene (10 mL) and the solution was stirred at 70 °C for 3 h. The solid was isolated by filtration and washed with toluene (10 mL). The resulting MAO–silica was re-dispersed in toluene (10 mL), following which the prepared complex (150  $\mu\text{mol}$ ) was added. After stirring at 70 °C for 1 h, the solid was isolated by filtration and washed with toluene (20 mL). The residual solvents were completely removed using a vacuum line to obtain the supported catalyst.

### 3.29. Ethylene/1-Hexene Polymerization

A bomb reactor (450 mL) was evacuated at 120 °C for 4 h and then purged with nitrogen gas. Hexane (300 mL) containing  $\text{Et}_3\text{Al}$  (0.20 mL) was added to the reactor, and the mixture was stirred for 1 h at 80 °C. Subsequently, the solution was removed using a cannula. The reactor was evacuated to remove any residual solvents. Next, the reactor was evacuated again at 120 °C for 4 h and recharged with nitrogen gas at atmospheric pressure. The reactor was then recharged with hexane (300 mL) containing 1-hexene (3.0 mL), and the temperature was set to 80 °C.  $\text{Et}_3\text{Al}$  (0.2 mL) dissolved in hexane (3.0 mL) was injected and, subsequently, fine particles of the prepared supported catalyst (6.0 mg) were injected into the reactor using a syringe dispersed in hexane (3.0 mL). Ethylene gas was charged to 20 bar

for a few seconds. The polymerization was performed for 30 min while maintaining the temperature at 80 °C and a constant pressure of 20 bar by feeding ethylene gas continuously. After the reactor was cooled to room temperature, the remaining ethylene gas was vented off and the generated polymer particles were collected by filtration.

### 3.30. X-ray Crystallography

Specimens of suitable quality and size were selected, mounted, and centered in the X-ray beam using a video camera. Reflection data were collected at 100 K on an APEX II CCD area diffractometer (Bruker) using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ). The hemisphere of the reflection data was collected as  $\varphi$  and  $\omega$  scan frames at  $0.5^\circ$  per frame and an exposure time of 10 s per frame. The cell parameters were determined and refined using the SMART program. Data reduction was performed using the SAINT software. The data were corrected for Lorentz and polarization effects. Empirical absorption correction was applied using the SADABS program. The structure was solved by direct methods and refined by the full matrix least-squares method using the SHELXTL package and the olex2 program with anisotropic thermal parameters for all non-hydrogen atoms. Crystallographic data for 9 (CCDC# 2130400) that were used in all calculations are as follows: C<sub>26.88</sub>H<sub>29.64</sub>Cl<sub>0.12</sub>SSiZr, M = 508.33, triclinic,  $a = 9.00050(10)$ ,  $b = 10.1721(2)$ ,  $c = 13.1285(2) \text{ \AA}$ ,  $\alpha = 90.6600(8)^\circ$ ,  $\beta = 103.7878(8)^\circ$ ,  $\gamma = 95.4360(8)$ ,  $V = 1161.36(3) \text{ \AA}^3$ , space group  $P-1$ ,  $Z = 2$ , and 4421 unique ( $R(\text{int}) = 0.0262$ ). The final  $wR_2$  was 0.0799 ( $I > 2\sigma(I)$ ).

## 4. Conclusions

A series of Me<sub>2</sub>Si-bridged thiophene-fused cyclopentadienyl fluorenyl *ansa*-zirconocene complexes was prepared, and a complex containing a bulky 2-methyl-4-(4-*tert*-butylphenyl) indenyl ligand was also synthesized by the substitution of the fluorenyl ligand. Analogues containing tBuO(CH<sub>2</sub>)<sub>6</sub>-tether, as well as a dinuclear congener, were also prepared by substituting the Me<sub>2</sub>Si bridge with a tBuO(CH<sub>2</sub>)<sub>6</sub>(Me)Si bridge or by connecting the two *ansa*-zirconocene units with a -(Me)Si(CH<sub>2</sub>)<sub>6</sub>Si(Me)- spacer. Because of their solubility in hexane, the complexes containing tBuO(CH<sub>2</sub>)<sub>6</sub>-tether and dinuclear complexes were isolated at high yields with complete removal of contaminant THF signals. The silica-supported catalysts prepared with the newly synthesized complexes containing 2,7-di(*tert*-butyl)fluorenyl ligand showed up to two times higher productivity compared to that prepared with the conventional (THI)ZrCl<sub>2</sub> (21–26 vs. 12 kg PE/g-(supported catalyst)). The as-synthesized supported catalysts also produced polymers with comparable molecular weights ( $M_w$ , 330–370 vs. 300 kDa), with increased 1-hexene contents (1.3 vs. 1.0 mol%) but with generated polymer particles with decreased bulk density (0.35 vs. 0.42 g/mL).

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12030283/s1>, Figures S1–S24: <sup>1</sup>H and <sup>13</sup>C NMR spectra of 1–26.

**Author Contributions:** Conceptualization, B.Y.L.; validation, H.K. and Y.Y.; formal analysis, J.L.; investigation, S.M.J., J.Y.P., Y.B.H. and J.W.B.; writing—original draft preparation, B.Y.L.; writing—review and editing, S.M.J. and J.W.B.; supervision, B.Y.L.; project administration, S.C.; funding acquisition, S.C. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was supported by GS Caltex and the Priority Research Centers Program (2019R1A6A1A11051471) through the National Research Foundation of Korea (NRF).

**Data Availability Statement:** All data are included in this article and supporting information.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Kaminsky, W. Discovery of Methylaluminoxane as Cocatalyst for Olefin Polymerization. *Macromolecules* **2012**, *45*, 3289–3297. [[CrossRef](#)]
2. Kaminsky, W. Polyolefin-nanocomposites with special properties by in-situ polymerization. *Front. Chem. Sci. Eng.* **2018**, *12*, 555–563. [[CrossRef](#)]
3. Zhang, H.; Zou, C.; Zhao, H.; Cai, Z.; Chen, C. Hydrogen-Bonding-Induced Heterogenization of Nickel and Palladium Catalysts for Copolymerization of Ethylene with Polar Monomers. *Angew. Chem. Int. Ed.* **2021**, *60*, 17446–17451. [[CrossRef](#)] [[PubMed](#)]
4. Kilpatrick, A.F.R.; Geddes, H.S.; Turner, Z.R.; Buffet, J.-C.; Goodwin, A.L.; O'Hare, D. Polymethylaluminoxane organic frameworks (sMAOF)—Highly active supports for slurry phase ethylene polymerisation. *Catal. Sci. Technol.* **2021**, *11*, 5472–5483. [[CrossRef](#)]
5. Zaccaria, F.; Zuccaccia, C.; Cipullo, R.; Budzelaar, P.H.M.; Vittoria, A.; Macchioni, A.; Busico, V.; Ehm, C. Methylaluminoxane's Molecular Cousin: A Well-defined and "Complete" Al-Activator for Molecular Olefin Polymerization Catalysts. *ACS Catal.* **2021**, *11*, 4464–4475. [[CrossRef](#)]
6. Hejazi-Dehaghani, Z.-A.; Arabi, H.; Thalheim, D.; Vidakovic, D.; Nekoomanesh Haghghi, M.; Veith, L.; Klapper, M. Organic Versus Inorganic Supports for Metallocenes: The Influence of Rigidity on the Homogeneity of the Polyolefin Microstructure and Properties. *Macromolecules* **2021**, *54*, 2667–2680. [[CrossRef](#)]
7. Antonov, A.A.; Bryliakov, K.P. Post-metallocene catalysts for the synthesis of ultrahigh molecular weight polyethylene: Recent advances. *Eur. Polym. J.* **2021**, *142*, 110162. [[CrossRef](#)]
8. Velthoen, M.E.Z.; Muñoz-Murillo, A.; Bouhmadi, A.; Cecius, M.; Diefenbach, S.; Weckhuysen, B.M. The Multifaceted Role of Methylaluminoxane in Metallocene-Based Olefin Polymerization Catalysis. *Macromolecules* **2018**, *51*, 343–355. [[CrossRef](#)]
9. Eo, S.C.; Lee, S.; Park, G.H.; Jeon, J.Y.; Lee, B.Y. Anchoring sulfonic acid on silica surface through SiC bond for immobilization of catalyst for polyketone synthesis. *Catal. Today* **2016**, *265*, 77–83. [[CrossRef](#)]
10. Qi, M.; Fu, Z.; Fan, Z. Immobilization of metallocene catalysts. *Prog. Chem.* **2014**, *26*, 737–748. [[CrossRef](#)]
11. Lee, B.Y.; Oh, J.S. Preparation of anchored metallocene complexes on dehydroxylated silica and their use in the polymerization of ethylene. *Macromolecules* **2000**, *33*, 3194–3195. [[CrossRef](#)]
12. Cecílio, D.M.; Fernandes, A.; Lourenço, J.P.; McKenna, T.F.L.; Ribeiro, M.R. Innovative route for the preparation of high-performance polyolefin materials based on unique dendrimeric silica particles. *Polym. Chem.* **2021**, *12*, 4546–4556. [[CrossRef](#)]
13. Werny, M.J.; Zarupski, J.; ten Have, I.C.; Piovano, A.; Hendriksen, C.; Friederichs, N.H.; Meirer, F.; Groppo, E.; Weckhuysen, B.M. Correlating the Morphological Evolution of Individual Catalyst Particles to the Kinetic Behavior of Metallocene-Based Ethylene Polymerization Catalysts. *J. Am. Chem. Soc.* **2021**, *1*, 1996–2008. [[CrossRef](#)]
14. Zanoni, S.; Nikolopoulos, N.; Welle, A.; Vantomme, A.; Weckhuysen, B.M. Early-stage particle fragmentation behavior of a commercial silica-supported metallocene catalyst. *Catal. Sci. Technol.* **2021**, *11*, 5335–5348. [[CrossRef](#)]
15. Yang, Q.; McDaniel, M.P. Comparison of support effects on phillips and metallocene catalysts. *Catalysts* **2021**, *11*, 842. [[CrossRef](#)]
16. Collins Rice, C.G.; Buffet, J.C.; Turner, Z.R.; O'Hare, D. Supported permethylindenyl titanium catalysts for the synthesis of disentangled ultra-high molecular weight polyethylene (disUHMWPE). *Chem. Commun.* **2021**, *57*, 8600–8603. [[CrossRef](#)]
17. Mehdiabadi, S.; Lhost, O.; Vantomme, A.; Soares, J.B.P. Ethylene Polymerization Kinetics and Microstructure of Polyethylenes Made with Supported Metallocene Catalysts. *Ind. Eng. Chem. Res.* **2021**, *60*, 9739–9754. [[CrossRef](#)]
18. Matsko, M.A.; Semikolenova, N.V.; Zakharov, V.A.; Soshnikov, I.E.; Shundrina, I.K.; Sun, W.H. Formation of branched polyethylenes by ethylene homopolymerization using LNiBr<sub>2</sub> homo- and heterogeneous precatalysts: Interpretation of the polymer structures in comparison with commercial LLDPE. *J. Appl. Polym. Sci.* **2021**, *138*, e50436. [[CrossRef](#)]
19. Kenyon, P.; Leung, D.W.J.; Lyu, M.; Chen, C.; Turner, Z.R.; Buffet, J.C.; O'Hare, D. Controlling the activity of an immobilised molecular catalyst by Lewis acidity tuning of the support. *J. Catal.* **2021**, *402*, 94–100. [[CrossRef](#)]
20. Wang, X.; Kang, W.; Li, G.; Zhang, P.; Jia, H.; Gao, D. Porous organic polymer/MMT hybrid supports for efficient metallocene catalysts. *J. Mater. Sci.* **2021**, *56*, 19253–19266. [[CrossRef](#)]
21. Brant, P.; Yakovlev, S.; Raney, M.; Narvaez, A. Discovery of Polyolefin Granule Products That Can Be Deconstructed into Individual, Fully Separable Grains Provides New Insights into Grain Growth and Material Design. *Macromolecules* **2021**, *54*, 2187–2201. [[CrossRef](#)]
22. Lamb, J.V.; Buffet, J.-C.; Turner, Z.R.; O'Hare, D. Ethylene Polymerization Using Zirconocenes Supported on Pentafluorophenyl-Modified Solid Polymethylaluminoxane. *Macromolecules* **2020**, *53*, 929–935. [[CrossRef](#)]
23. Lamb, J.V.; Buffet, J.C.; Turner, Z.R.; Khamnaen, T.; O'Hare, D. Metallocene Polyethylene Wax Synthesis. *Macromolecules* **2020**, *53*, 5847–5856. [[CrossRef](#)]
24. Bernardes, A.A.; Scheffler, G.L.; Radtke, C.; Pozebon, D.; dos Santos, J.H.Z.; da Rocha, Z.N. Supported metallocenes produced by a non-hydrolytic sol-gel process: Application in ethylene polymerization. *Colloids Surf. A Physicochem. Eng.* **2020**, *584*, 124020. [[CrossRef](#)]
25. Groch, P.; Bihun-Kisiel, A.; Piontek, A.; Ochedzan-Siodlak, W. Structural and Thermal Properties of Ethylene-Norbornene Copolymers Obtained Using Vanadium Homogeneous and SIL Catalysts. *Polymers* **2020**, *12*, 2433. [[CrossRef](#)] [[PubMed](#)]
26. Encarnacion, J.D.; Park, S.J.; Ko, Y.S. Polymerization of heterophasic propylene copolymer with Me<sub>2</sub>Si(2-Me-4-PhInd)<sub>2</sub>ZrCl<sub>2</sub> supported on SiO<sub>2</sub> and SiO<sub>2</sub>-MgCl<sub>2</sub> carriers. *Korean J. Chem. Eng.* **2020**, *37*, 380–386. [[CrossRef](#)]
27. Bae, S.M.; Jeong, S.M.; Baek, J.W.; Lee, H.J.; Kim, H.; Yoon, Y.; Chung, S.; Lee, B.Y. Dinuclear metallocene complexes for high-performance supported catalysts. *Eur. Polym. J.* **2021**, *144*, 110243. [[CrossRef](#)]

28. Nifant'ev, I.E.; Ivchenko, P.V.; Vinogradov, A.A. Heterocycle-fused cyclopentadienyl metal complexes: Heterocene synthesis, structure and catalytic applications. *Coord. Chem. Rev.* **2021**, *426*, 213515. [[CrossRef](#)]
29. Nifant'ev, I.E.; Ivchenko, P.V. Synthesis of Heteroarene-Fused Cyclopentadienes and Related Compounds Suitable for Metallocene Preparation. *Adv. Synth. Catal.* **2020**, *362*, 3727–3767. [[CrossRef](#)]
30. Huang, L.; Liu, Z.; Zhang, Y.; Wu, C.; Cui, D. Ethylene-Triggered Regioselectivity Switch of Dimethylbutadiene in Their Copolymerization: Formation of “Plastic” Rubber and Mechanism. *ACS Catal.* **2022**, *12*, 953–962. [[CrossRef](#)]
31. Liu, Z.; Liu, B.; Zhao, Z.; Cui, D. Chemo- and Stereoselective Polymerization of Polar Divinyl Monomers by Rare-Earth Complexes. *Macromolecules* **2021**, *54*, 3181–3190. [[CrossRef](#)]
32. Wang, T.; Wu, C.; Cui, D. *cis*-1,4 Selective Copolymerization of Butadiene and Functionalized  $\alpha$ -Olefins via Polar Group Activation Mechanism. *Macromolecules* **2020**, *53*, 6380–6386. [[CrossRef](#)]
33. Park, J.H.; Do, S.H.; Cyriac, A.; Yun, H.; Lee, B.Y. Preparation of half-metallocenes of thiophene-fused and tetrahydroquinoline-linked cyclopentadienyl ligands for ethylene/ $\alpha$ -olefin copolymerization. *Dalton Trans.* **2010**, *39*, 9994–10002. [[CrossRef](#)]
34. Sampson, J.; Bruening, M.; Akhtar, M.N.; Jaseer, E.A.; Theravalappil, R.; Garcia, N.; Agapie, T. Copolymerization of Ethylene and Long-Chain Functional  $\alpha$ -Olefins by Dinuclear Zirconium Catalysts. *Organometallics* **2021**, *40*, 1854–1858. [[CrossRef](#)]
35. Liang, T.; Goudari, S.B.; Chen, C. A simple and versatile nickel platform for the generation of branched high molecular weight polyolefins. *Nat. Commun.* **2020**, *11*, 372. [[CrossRef](#)] [[PubMed](#)]
36. Liu, S.; Xing, Y.; Zheng, Q.; Jia, Y.; Li, Z. Synthesis of Anthracene-Bridged Dinuclear Phenoxyiminato Organotitanium Catalysts with Enhanced Activity, Thermal Stability, and Comonomer Incorporation Ability toward Ethylene (Co)polymerization. *Organometallics* **2020**, *39*, 3268–3274. [[CrossRef](#)]
37. Reinhart, E.D.; Jordan, R.F. Synthesis and Ethylene Reactivity of Dinuclear Iron and Cobalt Complexes Supported by Macrocyclic Bis(pyridine-diimine) Ligands Containing *o*-Terphenyl Linkers. *Organometallics* **2020**, *39*, 2392–2404. [[CrossRef](#)]
38. Khoshsefat, M.; Dechal, A.; Ahmadjo, S.; Mortazavi, S.M.M.; Zohuri, G.; Soares, J.B.P. Amorphous to high crystalline PE made by mono and dinuclear Fe-based catalysts. *Eur. Polym. J.* **2019**, *119*, 229–238. [[CrossRef](#)]
39. Chen, Q.; Suo, H.; Zhang, W.; Zhang, R.; Solan, G.A.; Liang, T.; Sun, W.H. 1,5-Naphthyl-linked bis(imino)pyridines as binucleating scaffolds for dicobalt ethylene oligo-/polymerization catalysts: Exploring temperature and steric effects. *Dalton Trans.* **2019**, *48*, 8264–8278. [[CrossRef](#)]
40. Khoshsefat, M.; Dechal, A.; Ahmadjo, S.; Mortazavi, M.M.; Zohuri, G.H.; Soares, J.B.P. Zn-assisted cooperative effect for copolymers made by heterodinuclear Fe–Ni catalyst. *ChemCatChem* **2020**, *12*, 5809–5818. [[CrossRef](#)]
41. Ryabov, A.N.; Voskoboynikov, A.Z. Constrained geometry complexes of titanium (IV) and zirconium (IV) involving cyclopentadienyl fused to thiophene ring. *J. Organomet. Chem.* **2005**, *690*, 4213–4221. [[CrossRef](#)]
42. Kim, S.; Park, J.; Song, B.; Yoon, S.-W.; Go, M.; Lee, J.; Lee, B. Preparation of Thiophene-Fused and Tetrahydroquinoline-Linked Cyclopentadienyl Titanium Complexes for Ethylene/ $\alpha$ -Olefin Copolymerization. *Catalysts* **2013**, *3*, 104–124. [[CrossRef](#)]
43. Lee, S.; Park, S.S.; Kim, J.G.; Kim, C.S.; Lee, B.Y. Preparation of “Constrained Geometry” Titanium Complexes of [1,2]Azasilinane Framework for Ethylene/1-Octene Copolymerization. *Molecules* **2017**, *22*, 258. [[CrossRef](#)] [[PubMed](#)]
44. Park, J.T.; Woo, B.W.; Yoon, S.C.; Shim, S.C. An efficient synthetic method of ansa-zirconocene dimethyl complexes via  $\text{Me}_2\text{ZrCl}_2$ . *J. Organomet. Chem.* **1997**, *535*, 29–32. [[CrossRef](#)]
45. Hong, B.K.; Lee, Y.H.; Han, C.W.; Choi, Y.Y.; Lee, K.S. Transition Metal Compound, Catalyst Composition Comprising the Same, and Method of Preparing Polyolefin. U.S. Patent 9963527B2, 8 May 2018.
46. Cho, K.J.; Lee, K.S.; Lee, S.M.; Hong, B.K.; Cho, M.S.; Kim, S.Y.; Han, C.W. Metallocene Compound. W.O. Patent 2016195423A1, 8 December 2016.
47. Alt, H.G.; Ernst, R. Dinuclear ansa zirconocene complexes as dual-site catalysts for the polymerization of ethylene. *J. Mol. Catal. A Chem.* **2003**, *195*, 11–27. [[CrossRef](#)]
48. Alt, H.G.; Ernst, R. Asymmetric dinuclear ansa zirconocene complexes with methyl and phenyl substituted bridging silicon atoms as dual site catalysts for the polymerization of ethylene. *Inorg. Chim. Acta* **2003**, *350*, 1–11. [[CrossRef](#)]
49. Bashir, M.A.; Vancompernelle, T.; Gauvin, R.M.; Delevoye, L.; Merle, N.; Monteil, V.; Taoufik, M.; McKenna, T.F.L.; Boisson, C. Silica/MAO/(*n*-BuCp) $_2$ ZrCl $_2$  catalyst: Effect of support dehydroxylation temperature on the grafting of MAO and ethylene polymerization. *Catal. Sci. Technol.* **2016**, *6*, 2962–2974. [[CrossRef](#)]
50. Tanaka, R.; Kawahara, T.; Shinto, Y.; Nakayama, Y.; Shiono, T. An Alternative Method for the Preparation of Trialkylaluminum-Depleted Modified Methylaluminoxane (dMMAO). *Macromolecules* **2017**, *50*, 5989–5993. [[CrossRef](#)]