

# Constrained geometry complexes of titanium (IV) and zirconium (IV) involving cyclopentadienyl fused to thiophene ring

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## Abstract

Constrained geometry complexes (CGCs) of titanium (IV) and zirconium (IV) containing isomeric cyclopentadienyls fused to thiophene fragment, i.e., 4,5-dimethylcyclopenta[*b*]thienyl and 5,6-dimethylcyclopenta[*b*]thienyl, have been prepared and unambiguously characterized. The molecular structure of the titanium complex  $[\eta^5\text{-}(5,6\text{-dimethylcyclopenta}[b]\text{thienyl})\text{SiMe}_2(\text{N}^i\text{Bu})\text{-}\eta^1\text{TiCl}_2$  was established by X-ray crystal structure analysis. Preliminary studies showed that the studied CGCs/MAO are active olefin polymerization catalysts.

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**Keywords:** Titanium; Zirconium; Cyclopentadienyl; Heterocycle; Polymerization

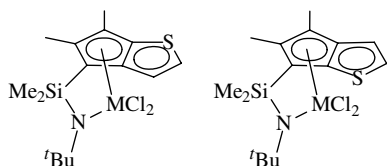
## 1. Introduction

During the last decade, a lot of attention has been paid to constrained geometry complexes (CGCs) of group 4 metals, which were found to be excellent catalysts for the copolymerization of ethene with  $\alpha$ -olefins, as well as homopolymerization of ethene producing branched polyethylenes (e.g., [1–22]). Another promising type of polymerization catalysts that was discovered quite recently is heterocenes [23–29], i.e., metallocenes containing cyclopentadienyls fused to heterocyclic fragments. Thus, the *ansa*-metallocenes containing Cp fused to thiophene ring were found to exhibit unprecedented activity in ethene and propene polymerization because of specific electronic properties of cyclopenta[*b*]thienyl ligands [26]. Though many complexes of the two heterocene families, *ansa*-heterocenes and “open” *bis*-cyclopentadienyl complexes containing thiophene fragment, have been described

in the public domain literature, this is not the case of CGCs including Cp fused to thiophene. These CGCs are mentioned in the claims of Fisher and Temme’s patent [23]. The respective complexes containing heteroanalogues of fluorenyl are described in a patent by Resconi et al. [30], as well as in their recent paper [31]. Quite recently, catalytic activity of a Ti CGC containing indenyl fused to thiophene fragment has been studied [32]. This complex, when activated by MAO, gave polypropylene with extremely high molecular weight ( $M_w > 2.8$  MD). It should be noted that the respective complexes containing Cp fused to thiophene fragment are of great interest for olefin polymerization due to recent findings that CGC catalytic efficiency can be enhanced by an increase in the electron density at the metal center [1,2,32–34]. The observed unprecedented activity of the *ansa*-heterocenes was suggested to result from the same effect [25,26]. In this contribution, we describe the synthesis, structure, and catalytic activity of two pairs of isomeric CGCs of Ti and Zr involving electron-donating cyclopenta[*b*]thienyl ligands, i.e.,

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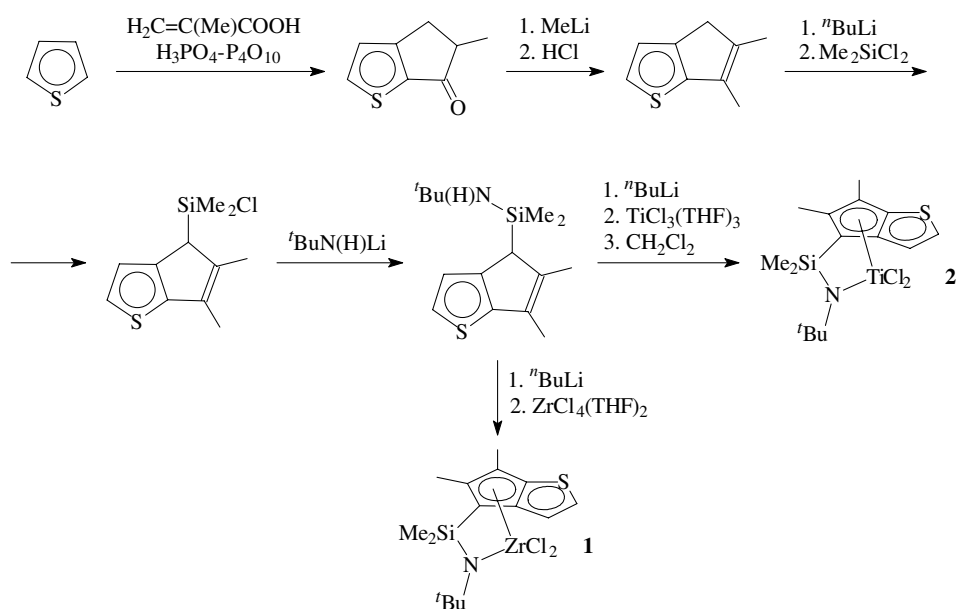


## 2. Results and discussion

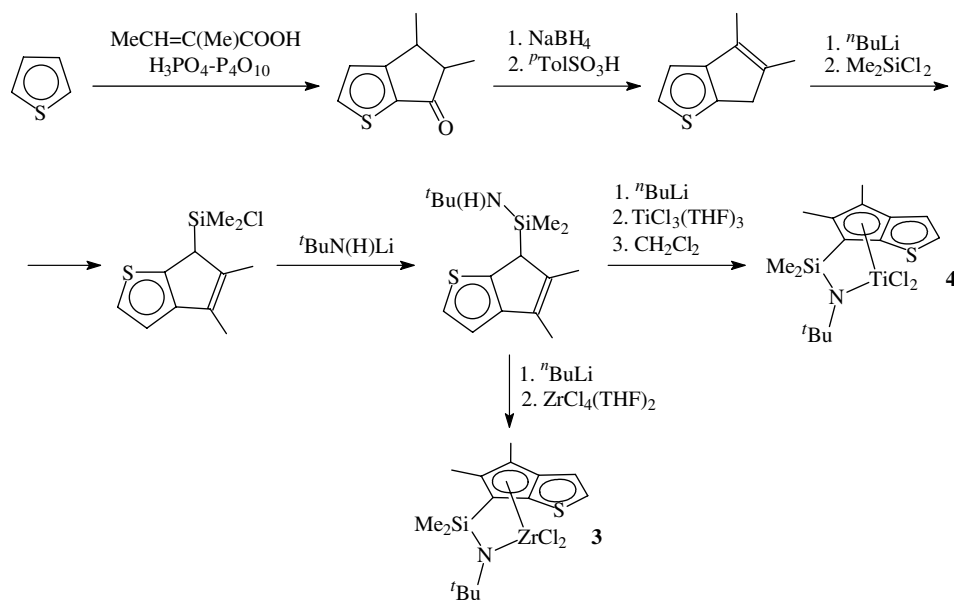
CGCs of Ti(IV) and Zr(IV) involving 5,6-dimethylcyclopenta[*b*]thienyl fragment were obtained as shown in Scheme 1. The one-pot acylation of thiophene by methacrylic acid followed by Nazarov cyclization in PPA-dichloromethane at 50 °C gave 5-methyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6-one in 40% yield [29,35]. The reaction of this ketone with MeLi followed by acidification by HCl gave 5,6-dimethyl-4*H*-cyclopenta[*b*]thiophene in 86% yield. The reaction of lithium salt of this thiopentalene with dichlorodimethylsilane in THF-hexanes resulted in chloro(5,6-dimethyl-4*H*-cyclopenta[*b*]thien-4-yl)dimethylsilane isolated in 70% yield. The reaction of this product with lithium salt of *tert*-butylamine in THF gave the desired chelating ligand, *N*-(*tert*-butyl)(5,6-dimethyl-4*H*-cyclopenta[*b*]thien-4-yl)dimethyl silylamine, isolated in 78% yield by fractional distillation in vacuum. This ligand was deprotonated with 2 equiv. of <sup>*n*</sup>BuLi, followed by treatment with 1 equiv. of ZrCl<sub>4</sub>(THF)<sub>2</sub> in ether-hexanes to give zirconium CGC **1**, which was isolated in 52% yield as a beige crystalline solid by recrystallization from hexanes.

Alternatively, the reaction of di-lithium salt of this ligand and 1 equiv. of TiCl<sub>3</sub>(THF)<sub>3</sub> in THF followed by oxidation of Ti(III) CGC by dichloromethane gave Ti(IV) CGC **2**, which was isolated in 35% yield as a brown solid by recrystallization from hexanes.

Constrained geometry complexes **3** and **4**, containing 4,5-dimethylcyclopenta[*b*]thienyl fragment, were prepared as shown in Scheme 2. In this case, the one-pot acylation coupled with Nazarov-like cyclization of thiophene using tiglic acid (instead of the earlier described multistage “malonate” synthesis [29]) and followed by reduction of 4,5-dimethyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6-one by NaBH<sub>4</sub> and acid-catalyzed dehydration gave 4,5-dimethyl-4*H*-cyclopenta[*b*]thiophene. In this way, 4,5-dimethyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6-one and a mixture of thiopentalenes were isolated in 90% and 74% yields, respectively. It should be noted that dehydration catalyzed by *para*-toluenesulfonic acid in toluene at reflux is accompanied by the partial isomerization of 4,5-dimethyl-4*H*-cyclopenta[*b*]thiophene into 4,5-dimethyl-6*H*-cyclopenta[*b*]thiophene. Then, the lithium salt of these thiopentalenes was treated with dichlorodimethylsilane in THF-hexanes to form chloro(4,5-dimethyl-6*H*-cyclopenta[*b*]thien-6-yl)dimethylsilane in 66% yield. This product was found to react readily with 1 equiv of lithium *tert*-butylamide to give *N*-(*tert*-butyl)(4,5-dimethyl-6*H*-cyclopenta[*b*]thien-6-yl)dimethylsilylamine. The bridging ligand, isolated in 75% yield by fractional distillation in vacuum, was deprotonated by 2 equiv of <sup>*n*</sup>BuLi in hexanes. The subsequent reaction of this di-lithium salt with 1 equiv of ZrCl<sub>4</sub>(THF)<sub>2</sub> in ether-hexanes gave zirconium CGC **3** in 45% yield as a yellowish



Scheme 1.



Scheme 2.

crystalline solid. Alternatively, the reaction of this dilithium salt and 1 equiv of  $\text{TiCl}_3(\text{THF})_3$ , followed by oxidation by dichloromethane gave Ti(IV) CGC **4** in 34% yield as a brown crystalline solid (crystallization from hexanes).

The molecular structure of complex **2** established by X-ray crystal structure analysis is shown in Fig. 1. Selected bond distances and angles are listed in Table 1. In this structure, the titanium atom is in a pseudotetrahedral environment defined by one  $\sigma$ -N silylamido ligand, one  $\eta^5$ -coordinated cyclopenta[*b*]thienyl ligand and two terminal chloride ligands. The amido nitrogen is planar (the sum of the bond angles around the N atom is  $359.6^\circ$ ) with  $\text{sp}^2$  hybridization. The similarity of the C(12)–N(1)–Ti(1) ( $128.3(3)^\circ$ ) and C(12)–N(1)–Si(1)

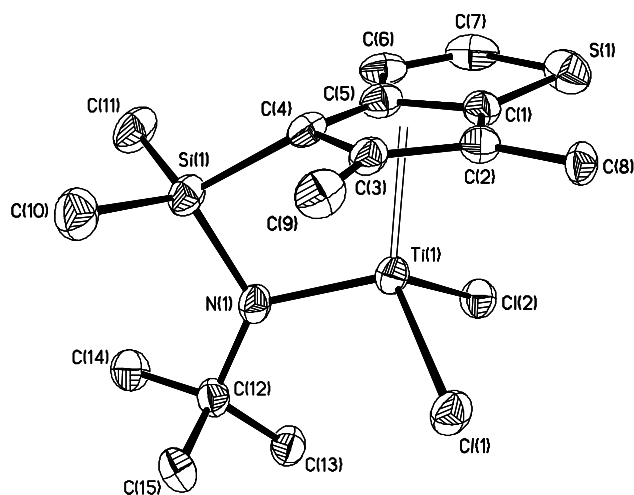


Fig. 1. Molecular structure of **2** with the non-hydrogen atom labeling scheme. The thermal ellipsoids are scaled to enclose 50% probability.

( $127.0(3)^\circ$ ) bond angles reflects the symmetric disposition of the *tert*-butyl substituent at the planar appended amido nitrogen. The plane including the Ti(1), N(1), Si(1), C(4), and C(12) atoms is perpendicular to the cyclopenta[*b*]thienyl ligand plane (angle between these planes is  $91.4^\circ$ ). The Ti(1)–N(1) distance ( $1.906(3)$  Å) is consistent with a  $\pi$ -bonding contribution from an interaction between the nitrogen  $\text{p}_\pi$  orbital and the appropriate vacant titanium  $\text{d}_\pi$  orbital [36]. However, the magnitude of this interaction is controlled both by the constrained geometry of the molecule and by the electronic and steric properties of the amido substituent, as observed in other complexes of this type  $[\text{Ti}\{(\eta^5\text{-C}_5\text{R}_4)\text{SiMe}_2(\eta^1\text{-NR})\}\text{Cl}_2]$  [33,37–46]. The Ti(1)–N(1) bond distance found in compound **2** is longer and therefore the  $\pi$ -bonding contribution is smaller than that found in unconstrained amido derivatives such as  $[\text{Ti}\{(\eta^5\text{-C}_5\text{H}_4\text{R})(\eta^1\text{-NH}^t\text{Bu})\}\text{Cl}_2]$  (R = H  $1.879(3)$  Å, R = Me  $1.871(5)$  Å) [47],  $[\text{Ti}\{(\eta^5\text{-C}_5\text{Me}_5)(\eta^1\text{-NH}^t\text{Bu})\}\text{Cl}_2]$  ( $1.877(4)$  Å) [48],  $[\text{Ti}\{(\eta^5\text{-C}_5\text{R}_5)(\eta^1\text{-N}^i\text{Pr}_2)\}\text{Cl}_2]$  (R = H  $1.865(2)$ , R = Me  $1.865(5)$  Å) [49],  $[\text{Ti}\{(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-N}(\text{SiMe}_3)_2)\}\text{Cl}_2]$  ( $1.879(2)$  Å) [50], ( $1.881(3)$  Å) [51], and  $[\text{Ti}\{(\eta^5\text{-C}_9\text{H}_7)(\eta^1\text{-NMe}_2)\}\text{Cl}_2]$  ( $1.864(4)$  Å) [52]. The presence of the  $\text{SiMe}_2$  bridge in **2** results in an appreciable decrease in the Cp(c)–Ti(1)–N(1) angle ( $109.0^\circ$ ) as compared to the values reported for the structurally similar unlinked monocyclopentadienyl group amido complexes ( $110.1$ – $129.5^\circ$ ) [47–52]. The constrained geometry of **2** imposed by the chelating  $[(\text{SC}_7\text{Me}_2\text{H}_2)\text{SiMe}_2(\text{N}^t\text{Bu})]^{2-}$  ligand is characterized by a considerable displacement ( $0.87$  Å) of the Si atom from the cyclopenta[*b*]thienyl ligand plane, as indicated by the Cp(c)–C(4)–Si(1) angle ( $152.4^\circ$ ), and results in the internal C(4)–Si(1)–N(1) and Si(1)–N(1)–Ti(1)

Table 1  
Selected bond distances and angles for **2**

Bond distances (Å)	
Ti(1)–Cl(1)	2.2725(17)
Ti(1)–Cl(2)	2.2643(18)
Ti(1)–N(1)	1.906(3)
Ti(1)–Cp(c) <sup>a</sup>	2.045
Ti(1)–C(1)	2.472(4)
Ti(1)–C(2)	2.459(4)
Ti(1)–C(3)	2.330(4)
Ti(1)–C(4)	2.259(4)
Ti(1)–C(5)	2.349(4)
Si(1)–N(1)	1.752(4)
Si(1)–C(4)	1.865(4)
Bond angles (°)	
Cl(1)–Ti(1)–Cl(2)	101.59(6)
N(1)–Ti(1)–Cl(1)	105.43(11)
N(1)–Ti(1)–Cl(2)	109.41(11)
Cl(1)–Ti(1)–Cp(c) <sup>a</sup>	116.1
Cl(2)–Ti(1)–Cp(c) <sup>a</sup>	114.7
N(1)–Ti(1)–Cp(c) <sup>a</sup>	109.0
N(1)–Si(1)–C(4)	91.11(17)
Ti(1)–N(1)–Si(1)	104.31(16)
Ti(1)–N(1)–C(12)	128.3(3)
Si(1)–N(1)–C(12)	127.0(3)

<sup>a</sup> Cp(c) denotes the centroid of the cyclopentadienyl ring of the thioindenyl ligand.

bond angles 91.1(2)° and 104.3(2)°, respectively. The interesting structural feature of **2** is the coordination symmetry of the cyclopenta[*b*]thienyl ligand to the titanium atom. The cyclopentadienyl ring of this ligand is nonsymmetrically bound to the titanium atom. The titanium atom slips in the direction of the C(4) atom (toward  $\eta^3$  coordination), thus increasing the Ti(1)–C(1) (2.472(4) Å) and Ti(1)–C(2) (2.459(4) Å) bond distances and decreasing the Ti(1)–C(4) (2.259(4) Å) bond distance. The same structural feature was found in recently reported analogous complexes [Ti{(η<sup>5</sup>-C<sub>9</sub>H<sub>5</sub>R)SiMe<sub>2</sub>(η<sup>1</sup>-N<sup>t</sup>Bu)}Cl<sub>2</sub>] (R = OMe, C<sub>4</sub>H<sub>8</sub>N) [44]. This phenomenon appears to be purely electronic in nature.

Preliminary study of the titanium CGCs showed that **2** and **4**/MAO are active catalysts of ethylene polymerization and ethylene/1-octene copolymerization (Table 2). In ethylene polymerization, the activity of **2**/MAO, involving a more sterically open CGC, was found to be higher than the activity of **4**/MAO. Both catalysts

give high molecular weight polymers, with  $M_w$  equal to 1.7 and 1.3 MD for **2** and **4**/MAO, respectively, though the latter gives a relatively broad molecular weight distribution. Ethylene/1-octene copolymerization catalyzed by **2** and **4**/MAO is characterized by high octene-1 insertion (e.g., 19.7% 1-octene residues for the first catalyst). Interestingly, the activities of each catalyst in both polymerization reactions were found to be very close (slightly higher for copolymerization), though molecular weight is considerably higher for the ethylene homopolymerization reaction.

In conclusion, the first constrained geometry complexes of titanium (IV) and zirconium (IV) containing cyclopentadienyl fused to one thiophene fragment were successfully synthesized and unambiguously characterized, including by X-ray crystal structure analysis. The titanium complexes with MAO were found to exhibit high activity in ethylene polymerization and ethylene/octene-1 copolymerization.

### 3. Experimental

#### 3.1. General

All manipulations with the compounds, which are sensitive to both moisture and air, were performed in an atmosphere of thoroughly purified argon using a standard Schlenk technique or in a controlled atmosphere glove box (Vacuum Atmospheres Co.). Tetrahydrofuran was purified by distillation over LiAlH<sub>4</sub> and kept over sodium benzophenone ketyl. Hydrocarbon solvents were distilled and stored over CaH<sub>2</sub> or Na/K alloy. Methylene chloride and CD<sub>2</sub>Cl<sub>2</sub> were distilled and stored over CaH<sub>2</sub>. Chloroform-*d* was distilled over P<sub>4</sub>O<sub>10</sub> and stored over molecular sieves (3 Å). Thiophene (Aldrich), methacrylic acid (Acros), tiglic acid (Acros), ZrCl<sub>4</sub>(THF)<sub>2</sub> (Aldrich), TiCl<sub>3</sub>(THF)<sub>2</sub> (Aldrich), NaBH<sub>4</sub> (Aldrich), <sup>*n*</sup>BuLi in hexanes (Chemetall), and MeLi in ether (Merck) were used as obtained. Dichlorodimethylsilane (Merck) was distilled under argon before use. *tert*-Butylamine (Acros) was distilled and stored over CaH<sub>2</sub>. Analytical liquid chromatography was performed using a Waters Delta 600 HPLC system including a 996

Table 2  
Ethylene polymerization (PE) and ethylene/octene-1 co-polymerization (PEOC) results for Ti CGCs **2** and **4**

CGC	Run type <sup>a</sup>	Activity, g/mmol h atm	$M_w$	$M_n$	PDI	Co-monomer wt.%	m.p., °C
<b>2</b>	PE	2400	1,745,500	866,800	2.0	–	136
<b>4</b>	PE	1550	1,312,000	221,100	5.9	–	135
<b>2</b>	PEOC <sup>b</sup>	2995	412,850	178,600	2.3	19.7	95
<b>4</b>	PEOC <sup>b</sup>	1685	838,400	365,350	2.3	15.8	102

<sup>a</sup> 0.02 μmol of CGC, 9.98 μmol of MAO ([Zr]/[Al] = 1/500), 3.97 ml of toluene, 80 °C, 5 atm of ethylene.

<sup>b</sup> 638 μmol of octene-1.

Photodiode Array Detector and a  $4.6 \times 100$  mm Chromolith RP-18e cartridge column (Merck).  $^1\text{H}$  and  $^{13}\text{C}$  spectra were recorded with Bruker Avance-400 and Bruker DPX-300 spectrometers for 1–10% solutions in deuterated solvents. Chemical shifts for  $^1\text{H}$  and  $^{13}\text{C}$  were measured relative to TMS. C, H microanalyses were done using a CHN-O-Rapid analyzer (Heraeus).

### 3.2. 5-Methyl-4,5-dihydro-6H-cyclopenta[b]thiophen-6-one

To polyphosphoric acid (prepared from 660 g of  $\text{P}_4\text{O}_{10}$  and 460 g of 85%  $\text{H}_3\text{PO}_4$ ), a mixture of 62.5 ml (65.7 g, 0.78 mol) of thiophene and 65.6 ml (66.6 g, 0.77 mol) of methacrylic acid in 100 ml  $\text{CH}_2\text{Cl}_2$  was added for 2.5 h at 50 °C. This mixture was stirred at this temperature for 2 h and then poured into 1 kg of ice. The product was extracted with  $4 \times 150$  ml of methyl-*tert*-butyl ether. The combined extract was washed with a saturated aqueous solution of  $\text{Na}_2\text{CO}_3$ , dried over  $\text{K}_2\text{CO}_3$ , and evaporated to dryness. Fractional distillation gave a white solid, bp 110 °C/5 mm Hg. Yield 47.8 g (40%).

### 3.3. 5,6-Dimethyl-4H-cyclopenta[b]thiophene

To 243 ml (0.40 mol) of 1.62 M MeLi in ether, a solution of 47.8 g (0.31 mol) of 5-methyl-4,5-dihydro-6H-cyclopenta[b]thiophen-6-one in 350 ml of ether was added for 30 min at –80 °C. This reaction mixture was stirred for 1.5 h at room temperature. Then, 50 ml of 40% HCl was added dropwise at –10 °C. The resulting mixture was stirred for 40 min at room temperature. The organic layer was separated, and the aqueous layer was extracted with  $2 \times 100$  ml of methyl-*tert*-butyl ether. The combined extract was washed with a saturated aqueous solution of  $\text{Na}_2\text{CO}_3$ , dried over  $\text{K}_2\text{CO}_3$ , and evaporated to dryness. Fractional distillation gave a colorless liquid, bp 100 °C/13 mm Hg. Yield 40.4 g (86%).

### 3.4. Chloro(5,6-dimethyl-4H-cyclopenta[b]thien-4-yl)dimethylsilane

To a solution of 10.0 g (66.6 mmol) of 5,6-dimethyl-4H-cyclopenta[b]thiophene in 150 ml of THF 26.6 ml of 2.5 M (66.6 mmol)  $^t\text{BuLi}$  in hexanes was added dropwise under vigorous stirring over 30 min at –60 °C. This mixture was stirred over 2 h at 20 °C. Then, this solution was added dropwise for 3 h at ambient temperature to a solution of 23.5 ml (25.2 g, 200 mmol) of dichlorodimethylsilane in 50 ml of THF. The resulting mixture was stirred for 12 h at room temperature and then evaporated to dryness. Fractional distillation gave a yellowish liquid, bp 103 °C/0.4 mm Hg. Yield 11.4 g (70%).

### 3.5. N-(*tert*-Butyl)(5,6-dimethyl-4H-cyclopenta[b]thien-4-yl)dimethylsilylamine

To a solution of 12.4 ml (8.59 g, 117 mmol) of *tert*-butylamine in 60 ml of THF, 19.2 ml of 2.5 M (48.2 mmol)  $^t\text{BuLi}$  in hexanes was added over 10 min at –80 °C. The reaction mixture was slowly warmed to ambient temperature and stirred additionally for 30 min. This solution was added dropwise over 1 h at room temperature to a mixture of 11.4 g (48.2 mmol) of chloro(5,6-dimethyl-4H-cyclopenta[b]thien-4-yl)dimethylsilane and 80 ml of THF. The reaction mixture was stirred for 12 h and then evaporated to dryness. Fractional distillation gave a yellowish liquid, bp 135–137 °C/0.5 mm Hg. Yield 10.5 g (78%).

### 3.6. Complex 1

To a solution of 1.99 g (7.13 mmol) of N-(*tert*-butyl)(5,6-dimethyl-4H-cyclopenta[b]thien-4-yl)dimethylsilylamine in 25 ml of diethylether, 5.70 ml of 2.5 M (14.3 mmol)  $^t\text{BuLi}$  in hexanes was added over 5 min at 0 °C. This mixture was stirred for 3 h at room temperature. The resulting suspension was cooled to –90 °C, and 2.90 g (7.69 mmol) of  $\text{ZrCl}_4(\text{THF})_2$  was added. This mixture was stirred for 24 h at ambient temperature and then evaporated to dryness. To the residue, 25 ml of toluene was added, and the resulting mixture was stirred for 6 h at 70 °C. Then, this mixture was evaporated to dryness. The product was extracted with  $4 \times 30$  ml of hot hexanes using a glass frit (G4) funnel. The filtrate was evaporated to ca. 70 ml. Crystals precipitated from this solution at –24 °C were separated and dried in vacuum. Yield 1.62 g (52%) of a beige crystalline solid.

### 3.7. Complex 2

To a solution of 4.71 g (16.9 mmol) of N-(*tert*-butyl)(5,6-dimethyl-4H-cyclopenta[b]thien-4-yl)dimethylsilylamine in 450 ml of hexanes, 13.5 ml of 2.5 M (35.8 mmol)  $^t\text{BuLi}$  in hexanes was added dropwise over 10 min at room temperature. This mixture was additionally stirred for 50 h. The precipitate of the lithium salt was filtered off (G3), washed with  $3 \times 30$  ml of hexanes, and dried in vacuum. Then, this lithium salt was dissolved in 100 ml of THF, and the obtained solution was added in one portion to a solution of 6.26 g (16.9 mmol) of  $\text{TiCl}_3(\text{THF})_3$  in 450 ml of THF. This mixture was stirred for 24 h and then evaporated to dryness. The product was extracted with  $4 \times 250$  ml of hot hexanes using a glass frit (G4) funnel. Crystals precipitated from this filtrate at –24 °C were separated and dried in vacuum. Yield 2.36 g (35%) of a brown crystalline solid.

### 3.8. 4,5-Dimethyl-4,5-dihydro-6H-cyclopenta[b]thiophen-6-one

To polyphosphoric acid (prepared from 500 g of  $P_4O_{10}$  and 340 g of 85%  $H_3PO_4$ ), a mixture of 47.6 ml (50.0 g, 0.60 mol) of thiophene and 59.5 g (0.60 mol) of tiglic acid in 80 ml of  $CH_2Cl_2$  was added over 2.5 h at 50 °C. This mixture was stirred at this temperature for 2 h and then immersed into 1 kg of ice. The product was extracted with  $3 \times 300$  ml of methyl-*tert*-butyl ether. The combined extract was washed with saturated aqueous solution of  $Na_2CO_3$ , dried over  $K_2CO_3$ , and evaporated to dryness. Fractional distillation gave a colorless oil, bp 96–98 °C/2 mm Hg. Yield 89.3 g (90%).

### 3.9. A mixture of 4,5-dimethyl-4H-cyclopenta[b]thiophene and 4,5-dimethyl-6H-cyclopenta[b]thiophene

To a solution of 89.3 g (0.54 mol) of 4,5-dimethyl-4,5-dihydro-6H-cyclopenta[b]thiophen-6-one in 750 ml of THF-methanol (2:1, vol.) 28.6 g (0.75 mol) of  $NaBH_4$  was added in small portions under vigorous stirring for 1 h at 5 °C. This mixture was stirred overnight at ambient temperature and then added to ca. 1000  $cm^3$  of cold water. The organic layer was separated; the aqueous layer was extracted with  $2 \times 300$  ml of methyl-*tert*-butyl ether. The combined extract was dried over  $K_2CO_3$  and evaporated to dryness. To a hot solution of the residue in 1500  $cm^3$  of toluene, 0.5 g of *para*-toluenesulfonic acid was added. This mixture was refluxed for 15 min, cooled to room temperature (iced water bath), and passed through a short column with Silica Gel 60 (40–63  $\mu m$ , d 65 mm, l 150 mm). The column was additionally washed with hexanes to isolate the product. The obtained solution was evaporated to dryness. Fractional distillation gave a colorless oil, bp 56–58 °C/3 mm Hg. Yield 60.0 g (74%) of a yellowish liquid.

### 3.10. Chloro(4,5-dimethyl-6H-cyclopenta[b]thien-6-yl)dimethylsilane

To a solution of 10.0 g (66.6 mmol) of a mixture of 4,5-dimethyl-4H-cyclopenta[b]thiophene and 4,5-dimethyl-6H-cyclopenta[b]thiophene in 150 ml of THF, 26.6 ml of 2.5 M (66.6 mmol)  $nBuLi$  in hexanes was added dropwise over 30 min at –60 °C. This mixture was additionally stirred for 2 h at room temperature and then added dropwise over 3 h to a solution of 23.7 ml (25.2 g, 200 mmol) of dichlorodimethylsilane in 50 ml of THF. The resulting mixture was stirred for 12 h at ambient temperature and then evaporated to dryness. Fractional distillation gave a yellowish liquid, bp 83–85 °C/0.2 mm Hg. Yield 10.7 g (66%).

### 3.11. N-(*tert*-Butyl)(4,5-dimethyl-6H-cyclopenta[b]thien-6-yl)dimethylsilanamine

To a solution of 11.7 ml (8.12 g, 111 mmol) of *tert*-butylamine in 60 ml of THF, 17.6 ml of 2.5 M (44.1 mmol)  $nBuLi$  in hexanes was added dropwise over 10 min at –80 °C. This mixture was additionally stirred for 30 min at room temperature. The resulting solution was added over 1 h to a solution of 10.7 g (44.1 mmol) of chloro(4,5-dimethyl-6H-cyclopenta[b]thien-6-yl)dimethylsilane in 80 ml of THF. This mixture was additionally stirred for 12 h and then evaporated to dryness. Fractional distillation gave a yellowish liquid, bp 110–113 °C/0.3 mm Hg. Yield 9.26 g (75%).

### 3.12. Complex 3

To a solution of 2.15 g (7.69 mmol) of N-(*tert*-butyl)(4,5-dimethyl-6H-cyclopenta[b]thien-6-yl)dimethylsilanamine in 40 ml of diethylether, 6.15 ml of 2.5 M (15.4 mmol)  $nBuLi$  in hexanes was added dropwise over 5 min at 0 °C. This mixture was additionally stirred for 24 h at ambient temperature. The resulting suspension was cooled to –30 °C, and 2.90 g (7.69 mmol) of  $ZrCl_4(THF)_2$  was added. This mixture was stirred for 24 h at room temperature and then evaporated to dryness. The crude product was extracted with 100 ml of toluene. The extract was filtered through glass frit (G4) and evaporated to dryness. The residue was extracted with  $5 \times 20$  ml of hot hexanes. The filtrate was filtered through a glass frit (G4) and evaporated to ca. 40 ml. Crystals precipitated at –24 °C were separated and dried in vacuum. Yield 1.53 g (45%) of a yellowish crystalline solid.

### 3.13. Complex 4

To a solution of 4.41 g (15.8 mmol) of N-(*tert*-butyl)(4,5-dimethyl-6H-cyclopenta[b]thien-6-yl)dimethylsilanamine in 450 ml of hexanes, 12.6 ml of 2.5 M (31.6 mmol)  $nBuLi$  in hexanes was added dropwise over 10 min. This mixture was additionally stirred for 50 h. The precipitate of lithium salt was separated, washed with  $3 \times 30$  ml of hexanes, and dried in vacuum. Then, this lithium salt was dissolved in 100 ml of THF and added in one portion to a solution of 5.85 g (15.8 mmol) of  $TiCl_3(THF)_3$  in 450 ml of THF. This mixture was stirred for 24 h at room temperature and then evaporated to dryness. The crude product was extracted with  $4 \times 250$  ml of hot hexanes using a glass frit (G4) funnel. Crystals precipitated from the filtrate at –24 °C were separated and dried in vacuum. Yield 2.12 g (34%) of a brown crystalline solid.

### 3.14. Crystal structure determination

A single crystal of **2** ( $C_{15}H_{23}Cl_2N_2SSiTi$ ,  $M = 396.29$ ) obtained by low-temperature ( $-30\text{ }^\circ\text{C}$ ) crystallization of this complex from hexane solution is monoclinic, space group  $P2_1/c$ ; at  $T = 110\text{ K}$ ,  $a = 12.698(8)$ ,  $b = 10.111(8)$ ,  $c = 14.763(11)\text{ \AA}$ ,  $\beta = 105.486(16)^\circ$ ,  $V = 1827(2)\text{ \AA}^3$ ,  $Z = 4$ ,  $d_c = 1.441\text{ g/cm}^3$ ,  $F(0\ 0\ 0) = 824$ ,  $\mu = 0.934\text{ mm}^{-1}$ . Data were collected on a Bruker SMART 1000 CCD diffractometer ( $\lambda$  (Mo  $K\alpha$ ) radiation, graphite monochromator,  $\theta$  and  $\phi$  scan modes,  $\theta_{\max} = 28^\circ$ ) and corrected for Lorentz and polarization effects and for absorption [54]. The structure was determined by direct methods and by full-matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined in the riding model with fixed thermal parameters ( $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for the  $\text{CH}_3$  groups and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for the other groups). The final  $R$  factors are  $R_1 = 0.0558$  for 2129 independent reflections with  $I > 2\sigma(I)$  and  $wR_2 = 0.1183$  for all 4414 independent reflections. All calculations were carried out using the SHELXTL (PC Version 5.10) program package [55].

### 3.15. Olefin polymerization studies

Transition metal compound (TMC) solutions (0.2 mmol/l) were typically prepared using toluene. Solvents, polymerization grade toluene and hexanes, were supplied by ExxonMobil Chemical Co. and thoroughly dried and degassed prior to use. 1-Octene (98%, Aldrich) was dried by stirring over NaK overnight followed by filtration through basic alumina (Brockman Basic 1, Aldrich). Polymerization grade ethylene was used and was further purified by passage through a series of columns: a 500-cm<sup>3</sup> Oxyclear<sup>®</sup> cylinder from Labclear (Oakland, CA), followed by a 500-cm<sup>3</sup> column packed with dried 3 Å molecular sieves (Aldrich), and a 500-cm<sup>3</sup> column packed with dried 5 Å molecular sieves (Aldrich). MAO (methylalumoxane, 10 wt% in toluene) was purchased from Albemarle and was used as a 1 wt% in toluene solution. Micromoles of MAO reported in the experimental section reflect the content of aluminum in MAO. The formula weight of MAO is 58.0 g/mol. Polymerizations were conducted in an inert atmosphere ( $\text{N}_2$ ) drybox using autoclaves equipped with an external heater for temperature control, glass inserts (internal volume of the reactor = 23.5 mL), septum inlets with a regulated supply of nitrogen and ethylene, and disposable PEEK mechanical stirrers (800 RPM). The autoclaves were conditioned by purging with dry nitrogen at 110 or 115 °C for 5 h and then at 25 °C for 5 h. The reactor was purged with ethylene. Toluene, 1-octene, and MAO were added via syringe at room temperature and atmospheric pres-

sure. The reactor was then brought to process temperature (80 °C) and charged with ethylene to the required pressure (75 psig = 517.1 kPa) under stirring at 800 RPM. The TMC (0.02  $\mu\text{mol}$ ) was added via syringe with the reactor at process conditions. Amounts of reagents not specified above are given in Table 1. Ethylene was allowed to enter (through the use of computer-controlled solenoid valves) the autoclaves during polymerization to maintain reactor gauge pressure ( $\pm 2$  psig). Reactor temperature was monitored and typically maintained within  $\pm 1\text{ }^\circ\text{C}$ . Polymerizations were halted by addition of approximately 50 psig of an  $\text{O}_2/\text{Ar}$  (5 mol%  $\text{O}_2$ ) gas mixture to the autoclaves over approximately 30 s. The polymerizations were quenched after a predetermined cumulative amount of ethylene had been added or after 20 min polymerization time. The reactors were cooled and vented. The polymer was isolated after the solvent was removed in vacuo.

For analytical testing, polymer sample solutions were prepared by dissolving polymer in 1,2,4-trichlorobenzene (TCB, 99+% purity, Aldrich) containing 2,6-di-*tert*-butyl-4-methylphenol (BHT, 99%, Aldrich) at 160 °C in a shaker oven for approximately 3 h. The typical concentration of polymer in a solution was between 0.4 and 0.9 mg/mL with a BHT concentration of 1.25 mg BHT per milliliter of TCB. Samples were cooled to 135 °C for testing. Molecular weights (weight average molecular weight ( $M_w$ ) and number average molecular weight ( $M_n$ )) and molecular weight distribution ( $\text{MWD} = M_w/M_n$ ), which is also sometimes referred to as the polydispersity index (PDI) of the polymer, were measured by gel permeation chromatography using a Symyx Technologies GPC equipped with an evaporative light scattering detector and calibrated using polystyrene standards. Samples were run in TCB at 135 °C (sample temperatures; 160 °C oven/columns) using three Polymer Laboratories PLgel 10  $\mu\text{m}$  Mixed-B 300  $\times$  7.5 mm columns in series. Thermal analysis was measured on a Symyx Technologies SAMMS (Sensory Array Modular Measurement System) instrument, which measures polymer melt temperatures via the  $3\omega$  technique. Samples for infrared analysis were subsequently analyzed on a Bruker Equinox 55 FTIR spectrometer equipped with a Pikes MappIR specular reflectance sample accessory. For ethylene-1-octene copolymers, the wt% copolymer is determined via measurement of the methyl deformation band at  $\sim 1375\text{ cm}^{-1}$ . The peak height of this band is normalized by the combination and overtone band at  $\sim 4321\text{ cm}^{-1}$ , which corrects for path length differences. The normalized peak height is correlated to individual calibration curves from  $^1\text{H}$  NMR data to predict the wt% copolymer content within a concentration range of  $\sim 2$  to 35 wt% for 1-octene. Typically,  $R^2$  correlations of 0.98 or greater are achieved.

#### 4. Supplementary material

Analytical and spectroscopic data for all newly prepared compounds. Crystallographic data for **2** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 271641. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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