

# Half-sandwich dibenzyl complexes of scandium: Synthesis, structure, and styrene polymerization activity

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## Abstract

Half-sandwich dibenzyl complexes of scandium have been prepared by stepwise treatment of scandium trichloride with lithium derivatives of silyl-functionalized tetramethylcyclopentadienes ( $C_5Me_4H$ )SiMe<sub>2</sub>R (R = Me, Ph) and benzyl magnesium chloride. The resulting complexes [Sc( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)(CH<sub>2</sub>Ph)<sub>2</sub>(THF)] and [Sc( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>SiMe<sub>2</sub>Ph)(CH<sub>2</sub>Ph)<sub>2</sub>(1,4-dioxane)] show structure related to that of the corresponding bis(trimethylsilylmethyl) compounds [Sc( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>SiMe<sub>2</sub>R)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF)]. The four-coordinate complexes display  $\eta^1$ -coordinated benzyl ligands without significant interaction of the ipso-carbon of the phenyl moiety. Conversion of [Sc( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)(CH<sub>2</sub>Ph)<sub>2</sub>(THF)] into the cationic species by treatment with triphenylborane in THF led to the formation of a stable charge separated complex [Sc( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)(CH<sub>2</sub>Ph)(THF)<sub>x</sub>][BPh<sub>3</sub>(CH<sub>2</sub>Ph)]. Benzyl cation formed using [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in toluene resulted in a moderately active syndiospecific styrene polymerization catalyst.

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**Keywords:** Scandium; Benzyl complexes; Styrene polymerization; Metallocene catalysis

## 1. Introduction

Half-sandwich complexes of scandium have attracted interest in the recent past as homogeneous polymerization catalyst precursors for various olefinic monomers [1,2]. A series of studies investigated the influence of ligand substitution patterns on the polymerization activity and selectivity of these complexes [2]. Being electronically and sterically more unsaturated when compared with metallocene compounds, the combination of a bulky cyclopentadienyl ligand with stabilizing alkyl groups such as CH<sub>2</sub>SiMe<sub>3</sub> or CH(SiMe<sub>3</sub>)<sub>2</sub> was instrumental in developing the chemistry of half-sandwich complexes of scandium [1]. Only few structurally characterized benzyl complexes of the rare-earth metals have been reported up to date [2e,3], in contrast to the numerous half-sandwich benzyl complexes of the group 4 metals [4]. We report here on

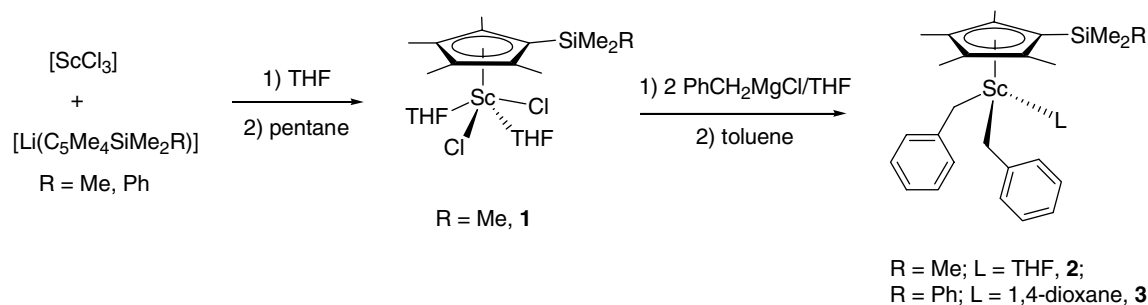
the synthesis and structural characterization of scandium half-sandwich dibenzyl complexes as well as their activity as styrene polymerization catalysts.

## 2. Results and discussion

### 2.1. Synthesis of dibenzyl complexes

Scandium half-sandwich complexes were obtained by salt metathesis of the corresponding lithium tetramethylcyclopentadienide [Li(C<sub>5</sub>Me<sub>4</sub>SiMe<sub>2</sub>R)] (R = Me, Ph) [5] with anhydrous scandium trichloride in THF. The dichloro complex [Sc( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Cl<sub>2</sub>(THF)<sub>2</sub>] (**1**) was isolated by extraction with pentane, whereas the SiMe<sub>2</sub>Ph substituted complex was prepared in situ. Addition of 2 equiv of Grignard reagent [(PhCH<sub>2</sub>)MgCl(THF)<sub>x</sub>] to **1** at low temperature followed by extraction with warm toluene afforded [Sc( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)(CH<sub>2</sub>Ph)<sub>2</sub>(THF)] (**2**). The slightly lower solubility of the analogous SiMe<sub>2</sub>Ph substituted complex required the precipitation of the magnesium chloride by addition of 1,4-dioxane from the concentrated

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Scheme 1.

THF solution. This work-up led to the isolation of the corresponding 1,4-dioxane containing complex  $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Ph})(\text{CH}_2\text{Ph})_2(1,4\text{-dioxane})]$  (**3**) (Scheme 1).

## 2.2. Structural characterization

The compounds have been characterized by NMR spectroscopic and analytical methods. Elemental analysis of the benzyl compounds **2** and **3** gave repeatedly poor results with largely differing values for the carbon content for identical crystalline samples. Complexometric titrations showed scandium content in agreement with the calculated values.

### 2.2.1. NMR spectroscopy

The dibenzyl complexes **2** and **3** show broad signals for the benzylic protons at ambient temperature (1.80, 2.14 ppm for **2**; 1.91, 2.23 ppm for **3**), partially overlapping with the signals of the methyl substituents on the cyclopentadienyl ring. Cooling of a sample of **2** to  $-40^\circ\text{C}$  resulted in splitting of the broad signal for the diastereotopic methylene groups into an AB pattern (1.87, 2.15 ppm,  $^2J_{\text{HH}} = 9.6\text{ Hz}$ , **2**). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data are in agreement with those of other structurally characterized scandium benzyl compounds and indicate  $\sigma$ -bonded benzyl groups in solution (chemical shift for benzyl  $\text{C}_{\text{ipso}}$  at 152.5 ppm for both **2** and **3**) [3,6].

The ether coordination at the scandium metal center is labile in solution at room temperature, resulting in broad

signals with a strong temperature dependence of the  $^1\text{H}$  NMR chemical shift for the methylene protons. Heating to temperature above ambient resulted in decomposition.

### 2.2.2. Crystal structure analysis

Recrystallization of the compounds **2** and **3** from toluene led to isolation of single crystals suitable for X-ray diffraction analysis. The solid state structures confirm the composition and structure derived from  $^1\text{H}$  NMR spectroscopic data in solution. Perspective views of complexes **2** and **3** are shown in Fig. 1, Table 1 contains details regarding the diffraction data and Table 2 compiles pertinent bond parameters.

Both complexes **2** and **3** show the typical piano stool geometry of half-sandwich complexes. The cyclopentadienyl ring is located on the apical position of a pseudo-tetrahedral coordination environment around the scandium metal center ( $\text{Sc}-\text{C}_{(\text{cent})}$  2.172 Å **2**, 2.163 Å for **3**), the two benzyl ligands and the donor (THF **2**, 1,4-dioxane **3**) are in the basal plane of the coordination sphere. The angles between these ligands are roughly equal in case of the dioxane donor ( $103.1 \pm 1.0^\circ$  for **3**), whilst the smaller steric demand of the THF donor results in slightly larger deviations ( $102.5 \pm 3.5^\circ$  for **2**). The  $\text{Sc}-\text{O}$  bond distances are similar in **2** and **3** ( $\text{Sc}-\text{O}(\text{THF})$  2.153(3) Å,  $\text{Sc}-\text{O}(\text{dioxane})$  2.139(2) Å), albeit compound **3** exhibits somewhat shorter scandium-ligand contacts. Due to the small size and the steric saturation of the scandium metal center, the benzyl ligands coordinate in a  $\sigma$ -bond fashion ( $\text{Sc}-\text{C}$  2.289(5),

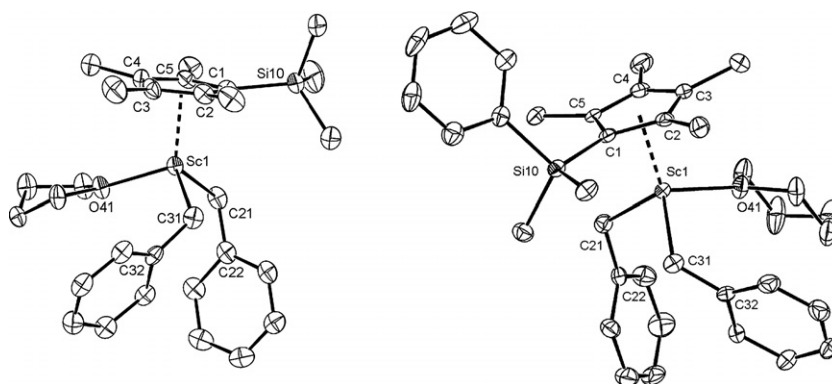


Fig. 1. Molecular structure of  $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{Ph})_2(\text{THF})]$  (**2**) and  $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Ph})(\text{CH}_2\text{Ph})_2(1,4\text{-dioxane})]$  (**3**).

Table 1  
Experimental data for the crystal structure determination of the complexes **2** and **3**

	<b>2</b>	<b>3</b>
<i>Crystal data</i>		
Formula	C <sub>30</sub> H <sub>43</sub> O <sub>2</sub> ScSi	C <sub>35</sub> H <sub>45</sub> O <sub>2</sub> ScSi
Formula weight	492.69	570.76
Crystal color	Colorless	Colorless
Crystal size, mm	0.46 × 0.35 × 0.13	0.24 × 0.16 × 0.09
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)
<i>a</i> (Å)	20.421(8)	8.8054(18)
<i>b</i> (Å)	9.330(4)	17.230(3)
<i>c</i> (Å)	15.101(6)	21.313(4)
$\beta$ (°)	101.143(10)	101.49(3)
<i>V</i> (Å <sup>3</sup> )	2823(2)	3168.7(11)
<i>Z</i>	4	4
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.322	0.299
<i>Data collection</i>		
<i>T</i> , K	130(2)	120(2)
$\lambda$ (Å)	0.71073	0.71073
$\theta$ Range	2.41–25.00	2.28–25.00
Index ranges	<i>h</i> , –23 to 24; <i>k</i> , –11 to 10; <i>l</i> , –11 to 17	<i>h</i> , –10 to 10; <i>k</i> , –16 to 20; <i>l</i> , –25 to 25
<i>Solution and refinement</i>		
Number of reflections measured	16505	21078
Number of independent reflections	4950	5591
Number of observed reflections	3407 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	3912 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))
Goodness-of-fit	1.077	1.030
Final <i>R</i> indices <i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> (observed data)	0.0868, 0.2081	0.0559, 0.1104
Final <i>R</i> indices <i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.1224, 0.2290	0.0899, 0.1233
Largest e-maximum, e-minimum, e Å <sup>-3</sup>	1.093, –0.538	0.315, –0.338

$$^a R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b R_w(F) = \frac{[\sum (F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}}$$

Table 2  
Selected bond distances [Å] and angles [°] of the complexes **2** and **3**

	<b>2</b>	<b>3</b>
Sc–C(21)	2.289(5)	2.279(3)
Sc–C(31)	2.267(5)	2.255(3)
Sc–O(41)	2.153(3)	2.139(2)
Sc–C(1)	2.476(5)	2.448(3)
Sc–C(2)	2.493(5)	2.466(3)
Sc–C(3)	2.494(5)	2.521(3)
Sc–C(4)	2.500(5)	2.496(3)
Sc–C(5)	2.476(5)	2.473(3)
C(21)–Sc–C(31)	105.38(19)	104.16(12)
C(21)–Sc–O(41)	97.96(15)	102.80(10)
C(31)–Sc–O(41)	104.17(15)	103.25(10)

2.268(5) **2**, 2.279(3), 2.255(3) Å for **3**) and no significant interaction with the ipso-carbon atom of the phenyl ring can be detected (Sc–C 3.184, 3.152 Å for **2**, 3.200, 3.245 Å for **3**). The  $\eta^1$ -coordination is also confirmed by the rather wide angle between the phenyl ring and the scan-

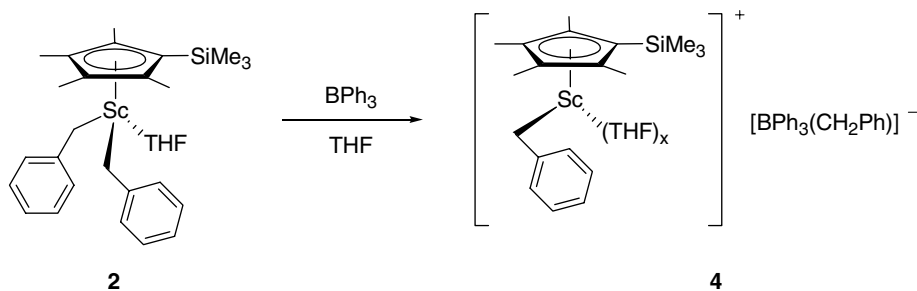
dium metal center (C<sub>ipso</sub>–C(21)–Sc 113.76°, 113.29° for **2**; 117.39°, 117.42° for **3**).

One benzyl-scandium distance is shorter in each complex ( $\Delta = 0.020$  Å **2**, 0.024 Å **3**), a feature also reported in the structurally related scandium  $\beta$ -diketiminato complex [Sc(L)(CH<sub>2</sub>Ph)<sub>2</sub>] (L = C{C(*t*Bu)N(2,6-*i*Pr–C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>}<sub>2</sub>) [**3g**], displaying an even larger difference with Sc–C distances of 2.203(7) Å and 2.265(6) Å. The analogous contact ion pair [Sc{(L')( $\eta^1$ -CH<sub>2</sub>Ph))}{( $\eta^6$ -PhCH<sub>2</sub>)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>}] (L' = C{C(Me)N(2,6-*i*Pr–C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>}<sub>2</sub>) on the other hand shows an intermediate Sc–C distance of 2.229(2) Å despite the charge effect in the cationic metal center [**3e**]. Other structurally characterized benzyl complexes of the rare-earth metals are [Ln( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(CH<sub>2</sub>Ph)<sub>2</sub>(THF)] (Ln = Y, Gd), [(Sm( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>( $\eta^6$ -CH<sub>2</sub>Ph)<sub>2</sub>K(THF)<sub>2</sub>)<sub>2</sub>] [**3c**], [Ln( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(CH<sub>2</sub>Ph)(THF)] (Ln = Ce, Sm) [**3a, 3b**], [(TMEDA)Y(CH<sub>2</sub>Ph)<sub>2</sub>Br<sub>2</sub>Li(TMEDA)] [**3d**], [Li{PhC(N-SiMe<sub>3</sub>)N(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>}<sub>2</sub>Y(CH<sub>2</sub>Ph)<sub>2</sub>], [(PhC(NSiMe<sub>3</sub>)N(CH<sub>2</sub>)<sub>3</sub>NMe<sub>2</sub>)<sub>2</sub>Y(CH<sub>2</sub>Ph)] [**3f**], [Y(C{CH<sub>2</sub>N(2,6-*i*Pr–C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>)(THF)<sub>2</sub>(CH<sub>2</sub>Ph)] [**3i**], and [La(CH<sub>2</sub>Ph)<sub>3</sub>(THF)<sub>3</sub>] [**3j**].

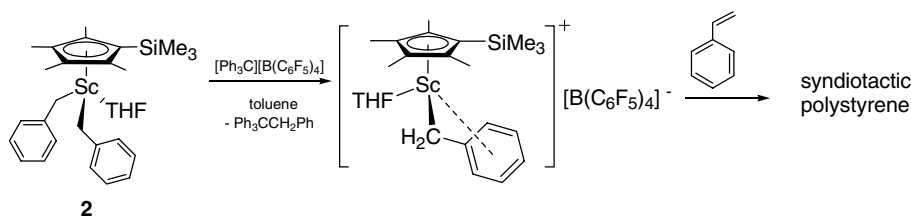
### 2.3. Styrene polymerization activity

For further investigation of the structure of the active species in polymerization catalysis, compound **2** has been converted into the corresponding cationic species. Addition of BPh<sub>3</sub> to a solution of **2** in THF led to fast transfer of one benzyl ligand to boron under formation of the THF solvated, charge separated ion pair [Sc( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)(CH<sub>2</sub>Ph)(THF)<sub>*x*</sub>][BPh<sub>3</sub>(CH<sub>2</sub>Ph)] (**4**). The NMR spectroscopic data indicate again a  $\sigma$ -bonded benzyl group remaining on the scandium metal center, while the other benzyl ligand is bound to boron (<sup>2</sup>*J*<sub>BH</sub> = 5.3 Hz; <sup>1</sup>*J*<sub>BC</sub> = 35.6 Hz) (Scheme 2).

The dibenzyl compound **2** has been tested as a catalyst for styrene polymerization (Scheme 3). Upon activation with 1 equiv of trityl borate [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] the resulting cationic species showed syndiospecific polymerization activity for styrene. The activity for **2** of 5.0 kg (sPS) mol(Sc)<sup>-1</sup> h<sup>-1</sup> was lower in comparison to the trimethylsilylmethyl complex [Sc( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF)] (6.3 × 10<sup>3</sup> kg(sPS) mol(Sc)<sup>-1</sup> h<sup>-1</sup>) under the same conditions [2g], [7]. The polystyrene obtained was syndiotactic according to <sup>13</sup>C NMR spectroscopic analysis and melting temperature of between 267 and 273 °C (DSC). The poorer styrene polymerization activity of **2** in comparison with the analogous trimethylsilylmethyl complex could be ascribed to the higher tendency of the benzyl ligand to coordinate to the metal center in the corresponding cationic species. Under polymerization conditions, in a weakly coordinating solvent such as toluene, the size of the active site on the metal center would thus be decreased compared to the alkyl complex and the monomer insertion impeded. Precedence for such a behavior was reported by Piers and co-workers for the scandium  $\beta$ -diketiminato dibenzyl complexes, which tend to form contact ion pairs upon addition of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in non-coordinating solvents



Scheme 2.



Scheme 3.

[3e]. The abstracted benzyl group remains in close proximity to the metal center by a  $\eta^6$ -bonding interaction.

Activation of the dichloro complex **1** with MAO under polymerization conditions analogous to the standard  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_3]$  catalyst system [8] resulted only in a small amount of atactic polystyrene [9]. Cationic rare earth metal complexes are often discussed as isostructural models of the active species in syndiospecific styrene polymerization  $[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}]^+$  [10]. The scandium system exhibits differing reactivity in the presence of excess of aluminum alkyl. We could recently show that the related bis(alkyl) complex  $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2(\text{C}_6\text{F}_5))(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ , which has polymerization activity comparable to the  $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ , also produces only small amounts of aPS in the presence of MAO [11].

### 3. Experimental

All operations were carried out under argon using standard Schlenk-line and glovebox techniques. Pentane was distilled from sodium/triglyme benzophenone ketyl, THF, and toluene from sodium benzophenone ketyl under argon. NMR spectra were recorded on Varian Unity-500 ( $^1\text{H}$ , 499.6 MHz;  $^{13}\text{C}$ , 125.6 MHz), Bruker Avance II 400 MHz ( $^1\text{H}$ , 400.1 MHz;  $^{13}\text{C}$ , 100.6 MHz), or Varian Mercury-200 ( $^1\text{H}$ , 200.1 MHz) spectrometers in  $[D_6]$ benzene,  $[D_8]$ THF,  $[D_8]$ toluene at 20 °C, unless stated otherwise; the chemical shifts were referenced to the residual solvent resonances. Combustion analysis of crystalline samples repeatedly gave poor results with inconsistent values from run to run. This difficulty is attributed to the extreme sensitivity of the material and has been described previously [3f,12]. Metal analysis was performed by complexometric

titration [13]. The substituted cyclopentadienes ( $\text{C}_5\text{Me}_4\text{H}$ )- $\text{SiMe}_2\text{R}$  ( $\text{R} = \text{Me}, \text{Ph}$ ) [5] were prepared according to literature procedures; benzyl magnesium chloride was obtained commercially as a THF solution.

#### 3.1. $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)\text{Cl}_2(\text{THF})_2]$ (**1**)

Anhydrous scandium trichloride (2.396 g, 16.0 mmol) was suspended in THF (50 mL) and a THF suspension of  $\text{Li}(\text{C}_5\text{Me}_4\text{SiMe}_3)$  (3.171 g, 16.0 mmol) in 40 mL was slowly added at  $-78$  °C. The reaction mixture was allowed to warm to room temperature over a period of two days. The solvent was removed in vacuo, the residue extracted with pentane ( $3 \times 30$  mL), and the extracts slowly cooled to  $-20$  °C. Colorless needles of  $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)\text{Cl}_2(\text{THF})_2]$  (**1**) were isolated (6.774 g, 14.9 mmol, 93.1%).  $^1\text{H}$  NMR (200 MHz,  $[D_6]$ benzene)  $\delta$ : 0.58 (s, 9H,  $\text{SiMe}_3$ ), 1.43 (t, 12H,  $\beta$ -THF), 2.23, 2.51 (s,  $2 \times 6\text{H}$ ,  $\text{C}_5\text{Me}_4$ ), 3.54 (t, 12H,  $\alpha$ -THF);  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$ : 2.3 ( $\text{SiMe}_3$ ), 12.4, 15.8 ( $\text{C}_5\text{Me}_4$ ), 25.6 ( $\beta$ -THF), 68.5 ( $\alpha$ -THF), 128.3 (ipso- $\text{C}_5\text{Me}_4$ ), 129.0, 132.7 ( $\text{C}_5\text{Me}_4$ ). Anal. Calc. for  $\text{C}_{20}\text{H}_{37}\text{Cl}_2\text{O}_2\text{ScSi}$  (453.46): C, 52.98; H, 8.22; Sc, 9.91. Found: C, 49.81; H, 7.62; Sc, 9.93%. The analysis indicate partial loss of THF upon standing to form  $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)\text{Cl}_2(\text{THF})]$ .

#### 3.2. $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{Ph})_2(\text{THF})]$ (**2**)

$[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)\text{Cl}_2(\text{THF})_2]$  (1.229 g, 2.71 mmol) was dissolved in THF (20 mL) and cooled to  $-78$  °C. Benzylmagnesium chloride (4.10 mL, 5.50 mmol; 20 wt% in THF) was slowly added via syringe, the reaction mixture was allowed to warm to room temperature, and stirred overnight. The volatiles were removed in vacuo and the

residue extracted with pentane (3 × 20 mL), the extracts concentrated and cooled to  $-40\text{ }^{\circ}\text{C}$ . Pale yellow crystals of **2** deposited (0.315 g, 0.64 mmol, 23.6%).  $^1\text{H}$  NMR (500 MHz,  $[\text{D}_8]$ toluene)  $\delta$ : 0.39 (s, 9H, SiMe<sub>3</sub>), 0.96 (s, 4H,  $\beta$ -THF), 1.82, 2.18 (s, 2 × 6H, C<sub>5</sub>Me<sub>4</sub>), overlapping with 1.80, 2.14 (m, 2 × 2H, CH<sub>2</sub>Ph), 3.12 (s, 4H,  $\alpha$ -THF), 6.70 (t,  $^2J_{\text{HH}} = 7.2$  Hz, 2H, *p*-Ph), 6.82 (d,  $^2J_{\text{HH}} = 7.6$  Hz, 4H, *o*-Ph), 7.04 (t,  $^2J_{\text{HH}} = 7.6$  Hz, 4H, *m*-Ph);  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$ : 2.4 (SiMe<sub>3</sub>), 11.6, 15.0 (C<sub>5</sub>Me<sub>4</sub>), 24.8 ( $\beta$ -THF), 58.8 (CH<sub>2</sub>Ph), 71.8 ( $\alpha$ -THF), 118.0 (ipso-C<sub>5</sub>Me<sub>4</sub>), 118.9, 125.1, 128.5 (*p*-, *o*-, *m*-Ph), 128.2, 129.2 (C<sub>5</sub>Me<sub>4</sub>), 152.5 (ipso-C of Ph);  $^1\text{H}$  NMR ( $[\text{D}_8]$ toluene,  $-40\text{ }^{\circ}\text{C}$ )  $\delta$ : 0.42 (s, 9H, SiMe<sub>3</sub>), 0.77 (s, 4H,  $\beta$ -THF), 1.73, 2.17 (s, 2 × 6H, C<sub>5</sub>Me<sub>4</sub>), 1.87, 2.15 (d,  $^1J_{\text{HH}} = 9.6$  Hz, 2 × 2H, CH<sub>2</sub>Ph), 3.12 (s, 4H,  $\alpha$ -THF), 6.70 (t,  $^2J_{\text{HH}} = 7.2$  Hz, 2H, *p*-Ph), 6.82 (d,  $^2J_{\text{HH}} = 7.3$  Hz, 4H, *o*-Ph), 7.04 (t,  $^2J_{\text{HH}} = 7.0$  Hz, 4H, *m*-Ph). Anal. Calc. for C<sub>30</sub>H<sub>43</sub>O<sub>5</sub>ScSi (492.69): Sc, 9.12. Found: Sc, 9.02%.

### 3.3. $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{Ph})(\text{CH}_2\text{Ph})_2(1,4\text{-dioxane})]$ (**3**)

*n*-Butyllithium (1.40 mL, 3.50 mmol; 2.5 M in hexanes) was added to a THF solution (30 mL) of (C<sub>5</sub>Me<sub>4</sub>H)SiMe<sub>2</sub>Ph (0.846 g, 3.30 mmol) at  $-78\text{ }^{\circ}\text{C}$  and subsequently warmed up to room temperature over a period of 1 h. The mixture was slowly added to a dispersion of scandium trichloride (0.500 g, 3.30 mmol) in THF (20 mL) at  $-78\text{ }^{\circ}\text{C}$  and stirred at room temperature overnight. The solvent was removed in vacuo, the residue extracted with pentane (3 × 20 mL) and toluene (20 mL) to give a yellow oil upon reduction of the solvent volume. THF (20 mL) was added, the solution cooled to  $-78\text{ }^{\circ}\text{C}$  and a solution of benzylmagnesium chloride (4.96 mL, 6.65 mmol; 20 wt% in THF) added dropwise. The solution was warmed up to room temperature for 3 h and the solution concentrated in vacuo. The oily residue was triturated with 1,4-dioxane (10 mL) to precipitate MgCl<sub>2</sub>(1,4-dioxane)<sub>2</sub>. Extraction with toluene (30 mL), removal of the solvent and recrystallization from toluene at  $-40\text{ }^{\circ}\text{C}$  gave yellow crystals of **3** (0.194 g, 0.34 mmol, 10.2%).  $^1\text{H}$  NMR (500 MHz,  $[\text{D}_6]$ benzene)  $\delta$ : 0.41 (s, 6H, SiMe<sub>2</sub>), 1.83, 2.18 (s, 2 × 6H, C<sub>5</sub>Me<sub>4</sub>), 1.91, 2.23 (d,  $^2J_{\text{HH}} = 8.9$  Hz, 2 × 2H, CH<sub>2</sub>Ph), 3.10, 3.55 (br s, 2 × 4H, dioxane), 6.77 (t,  $^2J_{\text{HH}} = 7.3$  Hz, 3H, *p*-Ph, *p*-CH<sub>2</sub>Ph), 6.91 (d,  $^2J_{\text{HH}} = 8.2$  Hz, 4H, *o*-CH<sub>2</sub>Ph), 7.00 (d,  $^2J_{\text{HH}} = 8.2$  Hz, 4H, *o*-Ph), 7.04 (t,  $^2J_{\text{HH}} = 7.3$  Hz, 2H, *m*-Ph), 7.11 (t,  $^2J_{\text{HH}} = 7.6$  Hz, 4H, *m*-Ph);  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$ : 2.4 (SiMe<sub>2</sub>), 11.7, 15.0 (C<sub>5</sub>Me<sub>4</sub>), 58.9 (CH<sub>2</sub>Ph), 67.9, 71.8 (dioxane), 118.9 (ipso-C<sub>5</sub>Me<sub>4</sub>), 125.1, 128.3, 129.3 (*p*-, *o*-, *m*-CH<sub>2</sub>Ph), 125.6, 128.3, 128.5 (*p*-, *o*-, *m*-Ph), 127.9, 128.1 (C<sub>5</sub>Me<sub>4</sub>), 152.5 (ipso-C of Ph). Anal. Calc. for C<sub>35</sub>H<sub>45</sub>O<sub>2</sub>ScSi (570.76): Sc, 7.88. Found: Sc, 7.76%.

### 3.4. $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{Ph})(\text{THF})_x][\text{BPh}_3(\text{CH}_2\text{Ph})]$ (**4**)

A solution of **2** (0.024 g, 0.05 mmol) in  $[\text{D}_8]$ THF (0.3 mL) was added to a solution of triphenylborane

(0.012 g, 0.05 mmol) in  $[\text{D}_8]$ THF (0.2 mL) and stored at room temperature for 2 h.  $^1\text{H}$  NMR (200 MHz,  $[\text{D}_8]$ THF)  $\delta$ : 0.90 (s, 9H, SiMe<sub>3</sub>), 1.95, 2.10 (s, 12H, C<sub>5</sub>Me<sub>4</sub>), 2.30 (s, 2H, CH<sub>2</sub>Ph), 2.47 (q,  $^2J_{\text{BH}} = 5.3$  Hz, 2H, CH<sub>2</sub>B), 6.51–7.20 (m, 25H, Ph).

### 3.5. Styrene polymerization

Toluene was dried over Na/benzophenone, distilled under argon, degassed in three freeze-pump-thaw cycles and stored over a sodium mirror. Styrene was dried over CaH<sub>2</sub> and stored in the glovebox at  $-40\text{ }^{\circ}\text{C}$ . Stock solutions (5 mM) of the Sc catalyst precursor **2**, the activator ([Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>][A], and (Al*i*Bu<sub>3</sub>; 50 mM stock solution) [Al] were prepared in toluene prior to use. In a typical polymerization experiment toluene (7 mL), Al*i*Bu<sub>3</sub> (1 mL [Al]), catalyst (1 mL [Sc]) and the activator (1 mL [A]) were successively combined and stirred for 1 min during which the solution changed its color from orange to light yellow or colorless. Styrene (~1 mL, weight recorded) was added and stirred rapidly for different periods of time (1–3 h, recorded). The polymerization was terminated by addition of acidified methanol (1 mL), the polymer washed with ethanol and dried under vacuum (~1 × 10<sup>-3</sup> mm Hg) at 60 °C overnight. Activities for **2**: 5.0 kg(sPS) mol(Sc)<sup>-1</sup> h<sup>-1</sup>. Samples were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy as well as DSC analysis, showing formation of highly syndiotactic polystyrene.  $^{13}\text{C}$  NMR (300 MHz,  $[\text{D}_2]$ tetrachloroethane)  $\delta$  40.6 (CH<sub>2</sub>CHPh), 43.7 (CH<sub>2</sub>CHPh), 125.7 (*p*-Ph), 127.7 (*m*-Ph), 128.0 (*o*-Ph), 145.4 (*ipso*-Ph). DSC melting endotherms of various samples were recorded between 267 and 273 °C.

### 3.6. X-ray crystallographic analysis

Crystal data were collected on a Bruker CCD area-detector diffractometer (graphite monochromated Mo K $\alpha$  radiation,) by use of  $\varphi$  and  $\omega$  scans. The SMART program package was used for the data collection and unit cell determination; processing of the raw frame data was performed using SAINT; absorption corrections were applied with SADABS [14]. The structures were solved by direct methods and refined against  $F^2$  using all reflections with the SHELXL-97 software package [15]. The non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed in calculated positions.

## 4. Supplementary material

CCDC 636934 and 636933 contain the supplementary crystallographic data for **2** and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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