# Synthesis, Characterization, and Polymerization Activity of the Scandium Half-Sandwich Complex $[Sc(\eta^5-C_5Me_4{SiMe_2(C_6F_5)})(CH_2SiMe_3)_2(THF)]^1)$

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Dedicated to Professor Glen B. Deacon on the Occasion of his 70<sup>th</sup> Birthday

**Abstract.** The scandium half-sandwich (bis)alkyl complex  $[Sc(\eta^5-C_5Me_4{SiMe_2(C_6F_5)})(CH_2SiMe_3)_2(THF)]$  has been prepared by  $\sigma$ -bond metathesis between  $[Sc(CH_2SiMe_3)_3(THF)_2]$  and  $C_5Me_4H{SiMe_2(C_6F_5)}$ . Structural characterization by single crystal X-ray diffraction revealed the typical piano-stool geometry for this type of complex. The addition of  $[Ph_3C][B(C_6F_5)_4]$  resulted in the formation of a half-sandwich alkyl cation which is an efficient catalyst for the syndiospecific polymerization of styrene in the presence of aluminium alkyls.

Keywords: Rare-earth metals; Half-sandwich compounds; Homogeneous catalysis

The structural investigation of rare-earth metal half-sandwich (bis)alkyl complexes has received attention in the last few years [1-3], due to their isostructural relationship with the cationic titanium(III) complex  $[Cp'TiMe]^+$ , which has been proposed as the active species in syndiospecific styrene polymerization by the commercially used titanium catalyst systems  $Cp'TiCl_3/MAO$  ( $Cp' = C_5H_5$  or  $C_5Me_5$ , MAO = methylalumoxane) [4]. The latter catalysts only show poor activity for the copolymerization of styrene with ethylene [5], resulting from the different oxidation states of the active species [6]. An improved system  $[Sc(\eta^5-C_5Me_4SiMe_3)(CH_2Si-Me_3)_2(THF)]/[Ph_3C][B(C_6F_5)_4]$  was recently reported showing high activity and stereoselectivity in the homo-/copolymerization of styrene with ethylene [7].

Interest in co- and terpolymers of styrene with a variety of  $\alpha$ -olefins stems from their improved mechanical properties during processing compared to the brittleness of syndiotactic polystyrene (sPS) [8]. Nonetheless it is a promising polymer material due to its high melting temperature and crystallinity as well as exceptional heat and chemical resistance [9].

Analogous rare-earth metal half-sandwich complexes have been prepared previously by our group [3, 10], thus prompting their rein-

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vestigation by extending the series of structurally characterized scandium, yttrium and lutetium compounds as precatalysts of type  $[(\eta^5-C_5Me_4{SiMe_2R})Ln(CH_2SiMe_3)_2(THF)]$  (Ln = Sc, Y, Lu) with different dimethylsilyl-substituents on the cyclopentadienyl ring including R = Me, Ph, 2-pyridyl, C<sub>6</sub>F<sub>5</sub>, 2-furyl, 2-(furyl-5-Me) [11]. These compounds show reasonably good stability as crystal-line solids as well as in solution. Catalyst activation with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in toluene results in highly sensitive, charge separated species [7]. We report on the synthesis and structural characterization of such a scandium half-sandwich (bis)alkyl complex and its activity in syndiospecific styrene polymerization.

# **Results and Discussion**

The scandium half-sandwich (bis)alkyl complex  $[Sc(\eta^5-C_5Me_4{SiMe_2(C_6F_5)})(CH_2SiMe_3)_2(THF)]$  1 was obtained by  $\sigma$ -bond metathesis in pentane between the scandium tris(trimethyl-silylmethyl) complex  $[Sc(CH_2SiMe_3)_3(THF)_2]$  and the substituted cyclopentadiene  $C_5Me_4H{SiMe_2(C_6F_5)}$  (Scheme 1) [2, 3]. Recrystallization from pentane at -40 °C afforded the complex as a colorless crystalline solid in good yield.



#### Scheme 1

Complex 1 has been fully characterized by analytical and spectroscopic methods. Determination of the solid-state structure by X-ray crystallography revealed a trigonal pyramidal structure as shown in Figure 1.



Fig. 1 Molecular structure of  $[Sc(\eta^5-C_5Me_4{SiMe_2(C_6F_5)})-(CH_2SiMe_3)_2(THF)]$  (1).

Selected bond distances /Å and angles /°: Sc(1)-C(24, 29) 2.201(2), 2.263(2); Sc(1)-O(34) 2.164(2); Sc(1)-C(1-5) 2.463(2)-2.542(2); C(24)-Sc(1)-C(29) 106.36(7); O(34)-Sc(1)-C(24) 100.96(7); O(34)-Sc(1)-C(29) 97.10(6).

The scandium half-sandwich complex 1 displays the commonly observed piano-stool geometry in the solid-state, with an  $\eta^5$ -coordinated cyclopentadienyl ring in the apical position of a trigonal pyramid and the remaining two alkyl ligands and the THF donor in the basal plane (Figure 1). Noteworthy is the preferential coordination of the THF donor trans to the silyl-substitutent of the cyclopentadienide ring. This arrangement has been observed before in the related 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)], which shows nearly identical structural features (Sc-O 2.158(2) Å, Sc-C 2.206(2), 2.240(2) Å; Sc-Cp<sub>cent</sub> 2.189 Å, *c.f.* 2.196 Å 1) [7].

Polymerization experiments of styrene, ethylene and  $\alpha$ -olefins with the catalyst system  $[Ln(\eta^5-C_5Me_4{SiMe_2R})(CH_2SiMe_3)_2(THF)]/$  $[Ph_3C][B(C_6F_5)_4]/AlR'_3$  reveal that the polymerization activity strongly depends on metal size (Ln = Sc > Y ~ Lu), but less on the nature of the substituent R (TMS ~ C\_6F\_5 > Ph > 2-py > 2-furyl). Moreover, they clearly demonstrate the crucial role of the aluminum alkyl cocatalysts AlR'\_3 [11]. Small alkyl or hydride groups, as in AlMe\_3, MAO, or Al*i*Bu\_2H, can potentially block the active site of the catalyst whereas AlEt\_3, Al*i*Bu\_3, and Al(CH\_2SiMe\_3)\_3 showed highly active catalyst systems. Whether this effect is attributable to varying scavenger qualities of the different aluminum alkyls or to their individual capability of stabilizing the active species still remains to be elucidated. Studies towards the structural elucidation of the corresponding cationic complexes are in progress.

# **Experimental Section**

All operations were carried out under argon using standard Schlenk-line and glovebox techniques. Pentane was distilled from sodium/triglyme benzophenone ketyl under argon. NMR spectra were recorded on Bruker Avance II (<sup>1</sup>H, 400.1 MHz; <sup>13</sup>C, 100.6 MHz) and Varian Mercury (<sup>19</sup>F, 188.1 MHz) spectrometers in [D<sub>6</sub>]benzene at 25 °C; the chemical shifts were referenced to the residual solvent resonances. Metal analysis was performed by complexometric titration [12].

# $[Sc(\eta^{5}-C_{5}Me_{4}{SiMe_{2}(C_{6}F_{5})})(CH_{2}SiMe_{3})_{2}(THF)]$ (1).

A solution of  $C_5Me_4H{SiMe_2(C_6F_5)}$  (0.70 g, 2.0 mmol) in pentane (10 mL) was added to  $[Sc(CH_2SiMe_3)_3(THF)_2]$  [13] (0.90 g, 2.0 mmol) and stirred at room temperature for 3 h. The solution was filtered and the solvent volume reduced to ~ 4 mL. Cooling to -40 °C gave colorless crystals of 1 (1.03 g, 1.6 mmol, 81 %).  $C_{29}H_{48}F_5OScSi_3$  (636.90) Sc 7.06 (calc. 6.98) %.

<sup>1</sup>H NMR δ = -0.27 (d, 4H, CH<sub>2</sub>SiMe<sub>3</sub>, 14.7 Hz), 0.27 (s, 18H, CH<sub>2</sub>SiMe<sub>3</sub>), 0.84 (t, 6H, SiMe<sub>2</sub>, 1.6 Hz), 1.18 (bs, 4H, β-THF), 1.78, 2.20 (s, 2 x 6H, C<sub>5</sub>Me<sub>4</sub>), 3.59 (t, 4H, α-THF, 6.4 Hz). <sup>13</sup>Ct<sup>1</sup>H} NMR δ = 2.6 (SiMe<sub>2</sub>), 4.3 (CH<sub>2</sub>SiMe<sub>3</sub>), 11.7, 14.8 (C<sub>5</sub>Me<sub>4</sub>), 25.1 (β-THF), 41.2 (b, Se-CH<sub>2</sub>), 71.2 (α-THF), 111.8 (ipso-C<sub>5</sub>Me<sub>4</sub>), 112.2 (ipso-C<sub>6</sub>F<sub>5</sub>), 124.7, 128.5 (C<sub>5</sub>Me<sub>4</sub>), 136.2, 148.8, 140.6, 143.1, 147.9, 150.3 (m, C<sub>6</sub>F<sub>5</sub>); <sup>19</sup>F NMR (C<sub>6</sub>D<sub>6</sub>) δ = -161.2 (m, 2F, o-C<sub>6</sub>F<sub>5</sub>), -152.6 (t, 1F, p-C<sub>6</sub>F<sub>5</sub>, 20.8 Hz), -126.8 (dd, 2F, m-C<sub>6</sub>F<sub>5</sub>, 9.8 Hz).

# Crystal structure determination of 1

A colorless fragment (0.48  $\times$  0.47  $\times$  0.43 mm) of 1 C<sub>29</sub>H<sub>48</sub>F<sub>5</sub>OScSi<sub>3</sub> (636.90 g mol<sup>-1</sup>) was selected for data collection at -153 °C. Monoclinic, P2<sub>1</sub>/c, a = 11.378(3) Å, b = 12.267(3) Å, c = 25.898(6) Å,  $\beta = 106.83(1)^{\circ}$ , V = 3459.9(15) Å<sup>3</sup>, Z = 4,  $\rho_{calcd} =$ 1.223 g cm<sup>-3</sup>,  $\mu = 0.363$  mm<sup>-1</sup>. X-ray diffraction data was collected on a Bruker CCD area-detector diffractometer with Mo-K $\alpha$ radiation (graphite monochromator,  $\lambda = 0.71073$  Å) using  $\varphi$  and  $\omega$  scans,  $\theta_{max} = 27.54^{\circ}$ . Indices:  $-14 \le h \le 14$ ,  $-15 \le k \le 15$ , -33<=1<=33; F(000) 1352; 50070 reflections collected, 7960 unique [R(int) = 0.0434], 7105 [I >  $2\sigma$ (I)]. 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]. Structure solution and refinement against  $F_0^2$  using direct methods with SHELXL-97 [15] led to  $R_1 = 0.0469 [I > 2\sigma(I)]$  and  $wR_2 =$ 0.1137 for all 7960 independent reflections.

Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre, CCDC 603507. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code +(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

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