Unprecedented dual behaviour of a half-sandwich scandium-based initiator for both highly selective isoprene and styrene polymerisation

Fanny Bonnet*, Cristina Da Costa Violante, Pascal Roussel, André Mortreux, Marc Visseaux*

Experimental and characterizing data

**Materials**: all operations were performed under dry argon by using Schlenk techniques. The solvents were dried over sodium/benzophenone ketyl, deoxygenated by distillation, and stored over molecular sieves (3A) in a glovebox. Styrene (99% from Aldrich) and isoprene (99% from Aldrich) were dried over calcium hydride, distilled twice, and stored over molecular sieves (3A) in a glovebox. Triisobutylaluminum (Al\textsubscript{3}Bu\textsubscript{3}) and trityl tetra(pentafluorophenyl)borate \([\text{CPh}_3][\text{B(C}_6\text{F}_5)_4]\) were purchased from Aldrich and used as received. \([\text{HNMe}_2\text{Ph}][\text{B(C}_6\text{F}_5)_4]\) dimethylphenylanilinium tetra(pentafluorophenyl)borate was purchased from Strem and used as received. \(\text{Sc(BH}_4)_3(\text{THF})_{1.5}\) was synthesized in THF as previously reported\(^1\).

**Polymer Analyses**: \(^1\)H and \(^13\)C NMR spectra of polyisoprenes and atactic PS were recorded on a Bruker Avance 300 instrument at 300 K in CDCl\(_3\). \(^1\)H and \(^13\)C NMR of syndiotactic polystyrenes (sPS) were recorded at 400 K in C\(_2\)D\(_2\)Cl\(_4\) on a Bruker AC 400. The chemical shifts were calibrated using the residual resonances of the solvent. Size exclusion chromatography of samples was performed in THF as an eluent at 40 °C (1 mL min\(^{-1}\)) with a Waters SIS HPLC pump, a Waters 410 refractometer, and Waters Styragel columns (HR2, HR3, HR4, and HR5E) calibrated with polystyrene standards. SEC analysis of sPS were conducted in trichlorobenzene as eluent at 135 °C using a Waters 150C PLUS device with coupled refractometer and viscosity detectors. DSC measurements were conducted under nitrogen on a Setaram 141 apparatus at a heating rate of 10 °C.min\(^{-1}\) from 20 to +300 °C using 20 mg samples in aluminum crucibles.
Synthesis and X-Ray structure of \((\text{C}_5\text{Me}_5)\text{Sc(BH}_4\text{)}_2(\text{THF})\) (2):

Sc(BH$_4$)$_3$(THF)$_{1.5}$ 1 (1 g, 5.06×10$^{-3}$ mol) and K(C$_5$Me$_5$) (0.882 g, 5.06×10$^{-3}$ mol) were weighed in a vessel in a glove box. The vessel was connected to the vacuum line and 50 mL of THF were distilled into the flask. After one night stirring at room temperature, a pale yellow solution was obtained with white salts. The THF was removed under vacuum and 50 mL of toluene were distilled into the vessel. The yellow solution was filtered and the salts were washed three times. Toluene was removed under vacuum and 30 mL of pentane were added leading to an off-white insoluble product (compound 2) and a yellow solution (compounds 3 and 4 see further). The solution was filtered and the off-white compound was washed three times with pentane. The solution was concentrated and some more off-white product precipitate, so the protocol was repeated three times since there was no more white compound crashing out (52% yield of 2). A crop of crystals were grown from a concentrated toluene solution. The $^1$H NMR spectrum in C$_6$D$_6$ at 293 K of the off-white compound obtained is typical of \((\text{C}_5\text{Me}_5)\text{Sc(BH}_4\text{)}_2(\text{THF})\) 2: $\delta = 2.019$ ppm (C$_5$Me$_5$, 15H, s); $\delta = 3.461$ and 0.9685 ppm (C$_4$H$_8$O, 2×4H, m); between 0.3 and 1.7 ppm (BH$_4$, 8H, very broad signal). Elemental analysis for ScC$_{14}$H$_{31}$B$_2$O (281.975 g mol$^{-1}$): C% 60.00 (calcd 59.66), H % 11.22 (calcd 11.01). X-Ray data: compound 2 (ScC$_{14}$H$_{31}$B$_2$O, Mw = 281.975) crystallizes in the orthorhombic space group Pmn2$_1$ with $a = 13.8226(4)$, $b = 8.0660(2)$, $c = 7.6377(2)$ Å, $\alpha = 90^\circ$, $V = 851.55(4)$ Å$^3$, and $\rho = 1.10722(5)$ g cm$^{-3}$ for $Z = 2$ (X Ray analysis performed at 100(1) K). Data were collected at 100(1) K on a Bruker Smart Apex CCD 4K system. The structure was solved by charge flipping methods using superflip software$^2$, and least-square refined with JANA2006 software$^3$. The model based on 3641 reflections ($I > 3.0\sigma(I)$, $R_{int} = 0.031$), total number of reflections = 38920, converged to a final $R_I = 3.12$ % ($wR_I = 3.47$%). Except H pertaining to BH$_4$ groups, all hydrogen atoms were placed in calculated positions. Others were located in difference Fourier maps and refined with isotropic thermal parameters. CCDC710423.

Compounds \((\text{C}_5\text{Me}_5)\text{Sc(BH}_4\text{)}_2\) (3) and \([(\text{C}_5\text{Me}_5)\text{Sc(BH}_4\text{)}\{\mu\text{-O(CH}_2\text{)}_3\text{CH}_3\}]_2\) (4) data:

These two products were obtained during the synthesis of compound 2 as described above, with isolated yield of 8.1% and 4.05% for 3 and 4, respectively. A crop of yellow crystals was obtained from the concentrated pentane solution obtained during synthesis of 2. $^1$H NMR data in C$_6$D$_6$ at 293 K: $\delta = 3.93$ ppm (CH$_2$, 2H, m); $\delta = 3.61$ ppm (CH$_2$, 2H, m); $\delta = 2.04$ ppm (C$_5$Me$_5$(4), 15H, s); $\delta = 1.89$ ppm (C$_5$Me$_5$(3), 30H, s); $\delta = 1.12$ ppm (CH$_2$, 2H, m); $\delta = 0.83$ ppm (CH$_3$, 3H, m); BH$_4$ groups display a really broad signal between 0.3 and 1.7 ppm. X-Ray
data: Compounds 3 and 4 \([\text{C}_{28}\text{H}_{56}\text{B}_2\text{O}_2\text{Sc}_2.2(\text{C}_{20}\text{H}_{34}\text{BSc})}\), \(\text{Mw} = 1196.796\) crystallizes in the monoclinic space group \(\text{P2}_1/\text{c}\) with \(a = 12.9989(11)\), \(b = 15.8168(14)\) \(c = 17.6308(14)\) Å, \(\beta = 106.550(5)°\), \(V = 3474.74(5)\) Å\(^3\), and \(\rho = 1.14351\) g cm\(^{-3}\) for \(Z = 2\) (X Ray analysis performed at 100(1) K). Data were collected at 100(1) K on a Bruker Smart Apex CCD 4K system. The structure was solved by charge flipping methods using superflip software\(^2\), and least-square refined with JANA2006 software\(^3\). The model based on 5276 reflections \((I > 3.0\ \sigma(I))\), \(\text{Rint} = 0.0862\), total number of reflections = 62611, converged to a final \(R1 = 4.23\ %\) \((wR1 = 4.15\%)\). Except H pertaining to BH\(_4\) groups, all hydrogen atoms were placed in calculated positions. Others were located in difference Fourier maps and refined with isotropic thermal parameters. CCDC710424.

Displacement ellipsoid plot (50\%) of 3 and 4. Hydrogen atoms partially omitted. Selected bond lengths (Å) and angles (°): Sc2-B2 = 2.557(3); Sc2-centroid = 2.158; Sc2-H60 = 2.057(15); Sc2-H59 = 2.047(12); Centroid-Sc2-centroid = 141.58°; Sc1-B1 = 2.347(3); Sc1-O1 = 2.0639(13) and 2.0814(14); Sc1-centroid = 2.157; Sc1-H26 = 2.099(12); Sc1-H25 = 2.065(19); Sc1-H27 = 2.299(15); Sc1-O1-Sc1 = 101.92°; O1-Sc1-O1 = 121.23°.

\(^1\)H NMR experiment of reaction of 2 with [HNMe\(_2\)Ph][B(C\(_6\)F\(_5\))\(_4\)] in \(d_8\)-THF: complex 2 (8 mg) was dissolved in 0.5 mL of \(d_8\)-THF in an NMR tube equipped with a valve (J. Young). 1 equivalent of [HNMe\(_2\)Ph][B(C\(_6\)F\(_5\))\(_4\)] (23 mg) was added and a reaction instantaneously occured with formation of bubbles (reaction with [CPh\(_3\)][B(C\(_6\)F\(_5\))\(_4\)] could not be studied as the resulting product with 2 immediately polymerizes THF). The obtained \(^1\)H NMR spectrum
shows the complete disappearance of the Me signals (Cp*) ring (1.95 ppm) and showed the quantitative formation of free PhNMe₂. A new signal relative to the Me (Cp*) appears slightly shifted at 2.05 ppm which is in accordance with the formation of the cation. ¹H NMR (300 MHz, d₈-THF, 25 °C, ppm): δ = 7.62-7.11 (m, 5 H, Ph), 2.93 (s, 3 H, NCH₃), 2.05 (s, 15 H, CpCH₃).

Study of the stability of complex 2 (¹H NMR experiment): Complex 2 (4 mg) was dissolved in 0.5 mL of C₆D₆ in an NMR tube equipped with a valve (J. Young). The tube was then heated for 3 d at 60 °C. The ¹H NMR spectrum of 2 after such a treatment shows no formation of any by-products which establishes that no comproportionation reactions occurred. See chemical shifts of 2 in the experimental section dealing with its synthesis. In d₈-THF no change was observed after prolonged stay at room temperature.

Typical styrene polymerisation experiment (run 3 given as an exemple): In a glove box under argon (H₂O and O₂ < 2 ppm), 6.1 mg of complex 2 were dissolved in 0.5 mL of dry and degassed toluene. 1 equivalent of tritylperfluorophenylborate [CPh₃][B(C₆F₅)₄] (20 mg, 2.17×10⁻⁵ mol) was then added under stirring and after several minutes an orange solution was obtained. 10 equivalents of Al¹Bu₃ (55 µL of a solution in toluene d = 0.786, 2.17×10⁻⁴ mol) were then added with a microsyringe and after several minutes the solution turned to pale yellow. 0.5 mL (4.35×10⁻³ mol) of styrene was then added, and the reaction was heated at 50 °C for 17 h. At the end of the reaction, a large amount of insoluble polymer was present in the Schlenk tube. The reaction was quenched by addition of some methanol drops. The polymer was washed in a large amount of methanol, filtered and dried under vacuum. The yield reached 80%, the average molecular weight of the obtained polymer was M_n = 6000, and the polydispersity index of 3.64. ¹H and ¹³C NMR analyses in C₂D₂Cl₄ at 400 K showed that the crude polystyrene obtained was 100% syndiotactic, without any previous extraction of the atactic fraction. The melting point of the polymer was 265 °C which is characteristic of syndiotactic polystyrene.

Polymerisation of styrene with half-scandocene synthesised in situ via the “B/A route”: In a glove box under argon (H₂O and O₂ < 2 ppm), 4.8 mg of complex 1 (2.42×10⁻⁵ mol) were dissolved in 0.55 mL of dry and degassed toluene. One equivalent of Cp*H (3.8 µL) was added, followed by 0.5 eq of butylethylmagnesium (BEM, 7.9 µL, 1.21×10⁻⁵ mol). 1 equivalent of tritylperfluorophenylborate [CPh₃][B(C₆F₅)₄] (22 mg) was then added under
stirring and after several minutes an orange solution was obtained. 10 equivalents of Al[i]Bu₃ (60 μL of a solution in toluene d = 0.786, 2.42×10⁻⁴ mol) were then added with a microsyringe and after several minutes the solution turned to pale yellow. 0.55 mL of styrene (4.8×10⁻³ mol) was then added, and the reaction was heated at 50 °C for 2 h 30. At the end of the reaction, a large amount of insoluble polymer was present in the Schlenk tube. The reaction was quenched by addition of some methanol drops. The polymer was washed in a large amount of methanol, filtered and dried under vacuum. The yield reached 62%, the average molecular weight of the obtained polymer was $M_n = 86600$, and the polydispersity index of 3.83. $^{13}$C NMR analyses in C₂D₂Cl₄ at 400K showed that 95% of the crude PS was purely syndiotactic.

**Typical isoprene polymerisation experiment (run 6 given as an example):** In a glove box under argon (H₂O and O₂ < 2 ppm), 2.8 mg of complex 2 (1×10⁻⁵ mol) were dissolved in 1 mL of dry and degassed toluene. 2 equivalents of [CPh₃][B(C₆F₅)₄] (18.4 mg, 2×10⁻⁵ mol) were then added under stirring and after several minutes an orange solution was obtained. 10 equivalents of Al[i]Bu₃ (in toluene d = 0.681, 25 μL, 1×10⁻⁴ mol) were then added with a microsyringe and after several minutes the solution turned to pale yellow. 3 mL of isoprene (0.03 mol) were then added, and the reaction was carried out at 20 °C for 1 min. At the end of the reaction the medium was completely solid. The reaction was quenched by addition of some methanol drops. The polymer was dissolved in toluene, poured in a large amount of methanol, filtered and dried under vacuum. The yield reached 99%, the average molecular weight of the obtained polymer is $M_n = 166700$ g mol⁻¹, and the polydispersity index of 2.2. $^1$H and $^{13}$C NMR analyses in CDCl₃ showed that the polyisoprene obtained was up to 96.3% cis-1,4 regular.

**Isoprene-styrene statistic copolymerisation experiment:** In a glove box under argon (H₂O and O₂ < 2 ppm), 3.4 mg of complex 2 (1.21×10⁻⁵ mol) were dissolved in 1 mL of dry and degassed toluene. 1 equivalents of [CPh₃][B(C₆F₅)₄] (11.2 mg, 1.21×10⁻⁵ mol) was then added under stirring and after several minutes an orange solution was obtained. 10 equivalents of Al[i]Bu₃ (in toluene d = 0.681, 30 μL, 1.21×10⁻⁴ mol) were then added with a microsyringe and after several minutes the solution turned to pale yellow. 0.5 mL of isoprene and 0.5 mL of styrene were then added and the reaction was carried out at 20 °C for 24 h. The reaction was quenched with methanol and the resulting polymer was dissolved in toluene, poured in a large amount of methanol, filtered and dried under vacuum. The yield was 92% taking only isoprene in account. The average molecular weight of the obtained copolymer could not be
determined as it was not completely soluble in THF. $^1$H NMR analyses in CDCl$_3$ showed the presence of cis-1,4-polyisoprene and 4.8% of inserted styrene units. ($^1$H spectrum of the copolymer can be obtained upon request)

$^{13}$C NMR spectrum in C$_2$D$_2$Cl$_4$ recorded at 400 K of purely syndiotactic polystyrene (run 3, table 1)

$^{13}$C NMR spectrum in C$_2$D$_2$Cl$_4$ recorded at 400 K of purely syndiotactic polystyrene (carbon ipso region, run 3 table 1)
References:

