

New divalent samarocenes for butadiene polymerisation: influence of the steric effect and the electron density on the catalytic activity

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Received 22 August 2003; accepted 8 October 2003

Abstract

Two new divalent samarocenes, $\text{Cp}_2^{\text{Pr}}\text{Sm}(\text{THF})$ (**1**) and $(\text{Cp}^{\text{Ph}_3})_2\text{Sm}(\text{THF})$ (**2**) ($\text{Cp}^{\text{Pr}} = \text{C}_5\text{Me}_4\text{Pr}$, $\text{Cp}^{\text{Ph}_3} = \text{H}_2\text{C}_5\text{Ph}_3\text{-1,2,4}$), were synthesized and characterized by ^1H NMR and elemental analysis. The activity of **1** and **2** as butadiene polymerisation catalysts was studied, in the presence of MAO and MMAO, and compared to this of $\text{Cp}_2^{\text{Sm}}\text{Sm}(\text{THF})_2$ (**3**) and $(\text{Cp}^{\text{H}^i})_2\text{Sm}$ (**4**) ($\text{Cp}^{\text{H}^i} = \text{C}_5\text{Me}_5$, $\text{Cp}^{\text{H}^i} = \text{C}_5\text{H}^i\text{Pr}_4$), in the same conditions. The **1**/MAO system presents the highest activity. The less active **2**/MAO system leads to a high *cis*-1,4 regular structure up to 97%. The MMAO cocatalyst is found very sensitive to the steric hindrance of the samarocenes: the activity decreases from **1**/MAO to **1**/MMAO, and no activity is observed in the case of complexes **2** and **4**, associated to MMAO. Complexes **1** and **2** can be both oxidized with AlMe_3 to give the corresponding Sm/Al bimetallics **1'** and **2'**, respectively. © 2003 Elsevier B.V. All rights reserved.

Keywords: Lanthanides; Diene polymerisation; Samarocenes

1. Introduction

Synthesis of polydienes is a field of major interest, because of their various applications in the rubber (tyres, adhesive, etc.) industry. Several Ziegler–Natta heterogeneous catalytic systems are able to polymerise conjugated dienes with a high *cis*-1,4 stereospecificity [1]. Traditional homogeneous d-block-metal catalysts associated to methylaluminoxane (MAO) are less stereospecific, but they allow a better control of molecular weight [2]. Rare earths systems become more and more appreciated in this specific field of catalysis [3,4]. They are known to give the highest rates of *cis*-1,4-polydiene (up to 99%) while providing a good control of molecular weight [5].

Organolanthanide chemistry has provided well-defined single site catalysts and particularly the traditional Cp_2LnR . These trivalent lanthanocenes are known as

efficient single component catalysts for the polymerisation of ethylene or acrylates [6]. However, these complexes have shown their limits, being inactive towards conjugated dienes. The divalent lanthanocenes are not active either [7], because of the formation of a stable $\text{Ln}(\text{III})(\eta^3\text{-allyl})$ complex [8]. Very recently, Wakatsuki and his co-workers [9] reported that polymerisation of butadiene was possible with $\text{Cp}_2\text{Sm}(\text{THF})_2$ (**3**) activated by aluminium derivatives: MMAO (modified methylaluminoxane containing both isobutyl and methyl groups [10]) or $\text{AlR}_3/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{R} = \text{Me}, \text{Et}, \text{tBu}$). The authors obtained regular *cis*-1,4 polybutadiene and discussed the reactivity of the catalytic system in regard to the nature of the aluminium reagent. They showed that the microstructure of the synthesized polybutadiene was more influenced than the activity of the dual component catalyst. It is noteworthy that the active species was a Sm(III) one.

In the course of our studies concerning the use of early organolanthanides for dienes polymerisation [11], we undertook to compare a set of lanthanocenes. We wanted to focus on the influence of the nature of the cyclopentadienyl ligands on the behaviour of Sm/Al

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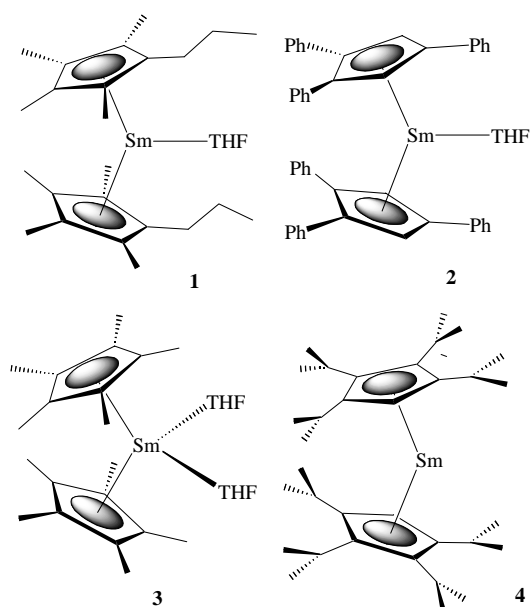
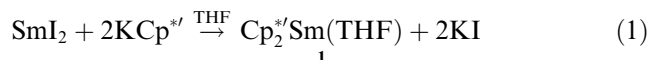
catalysts. With this aim, we synthesized two new divalent samarocenes, $\text{Cp}_2^*\text{Sm}(\text{THF})$ (**1**) and $(\text{Cp}^{\text{Ph}_3})_2\text{Sm}(\text{THF})$ (**2**), bearing the *n*-propyl-tetramethylcyclopentadienyl ($\text{Cp}^* = \text{C}_5\text{Me}_4\text{Pr}$) and the 1,2,4-triphenylcyclopentadienyl ($\text{Cp}^{\text{Ph}_3} = \text{H}_2\text{C}_5\text{Ph}_3\text{-1,2,4}$), respectively. The synthesis, and some reactivity of **1** and **2** are presented and discussed. Complexes **1**, **2** and **3**, but also the unsolvated $(\text{Cp}^{\text{Ph}_3})_2\text{Sm}$, **4** ($\text{Cp}^{\text{Ph}_3} = \text{C}_5\text{H}^i\text{Pr}_4$) described in a previous paper [12], have been tested for the polymerisation of 1,3-butadiene in the presence of MAO or MMAO. The influence of the nature of the cyclopentadienyl ligand on the activity of the complex and on the microstructure of the polymer is discussed.

2. Results and discussion

2.1. Samarocenes syntheses

We present here the synthesis of two new divalent samarocenes, $\text{Cp}_2^*\text{Sm}(\text{THF})$ (**1**) and $(\text{Cp}^{\text{Ph}_3})_2\text{Sm}(\text{THF})$ (**2**). The syntheses were all conducted in THF, using the procedure described in 1985 by Evans and co-workers [7] for the preparation of $\text{Cp}_2^*\text{Sm}(\text{THF})_2$ (**3**). Recently, some of us prepared in the same way the desolvated analogue $(\text{Cp}^{\text{Ph}_3})_2\text{Sm}$ (**4**). Scheme 1 summarizes the molecular structure of these divalent samarocenes, used thereafter for polymerisation experiments.

Complexes **1** and **2** were obtained from the reaction of 2 equivalents of the corresponding potassium ligand with SmI_2 , according to



Scheme 1. Molecular structure of samarocenes 1–4.

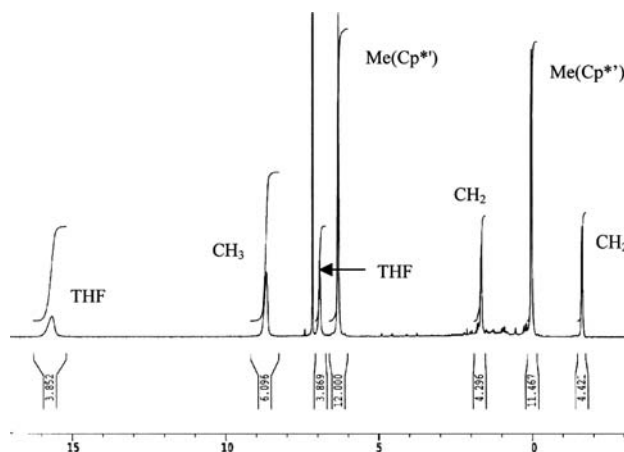
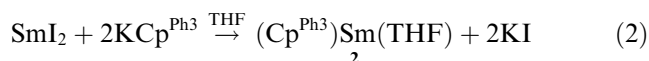


Fig. 1. ^1H NMR spectrum of **1** in C_6D_6 at 333 K.



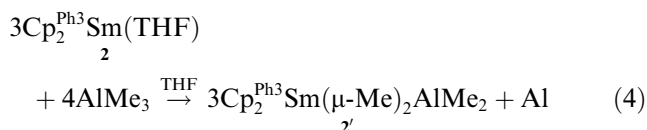
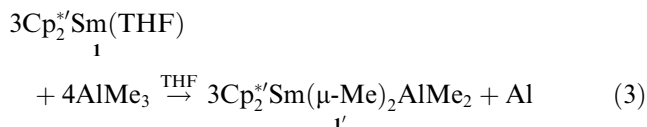
Contrarily to complex **3** which was isolated as a bis-tetrahydrofuran adduct, both new samarocenes contain only one THF molecule per Sm according to the elemental and ^1H NMR analyses.

The ^1H NMR spectrum of complex **1** is shown in Fig. 1. Despite the paramagnetism, one can easily attribute the resonances to the corresponding protons, as indicated. The presence of one unique THF, for both **1** and **2**, may be related to the higher steric hindrance induced by the propyl chain in **1**, and by the three phenyl groups in **2**.

One can note that the electron donating ability of Cp^{Ph_3} , bearing three withdrawing phenyl substituents, seems weaker than this of Cp^* , leading a priori to a better affinity towards THF. But the much larger size of the bulky ligand might preclude the coordination of more than one THF per Sm. As for complex **4**, the absence of THF was postulated as being the consequence of both steric and electronic saturation [12].

2.2. Oxidation of samarocenes 1 and 2

Wakatsuki showed that the bimetallic complex $[\text{Cp}^*\text{Sm}(\mu\text{-Me})_2\text{AlMe}_2]_2$ (**3'**) was efficient in butadiene polymerisation in the presence of $\text{AlR}_3/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{R} = \text{Me}, \text{Et}, \text{tBu}$) [9]. This bimetallic complex had been prepared by Evans et al. [13] upon an oxidizing/alkylating process of **3** with AlMe_3 . In preliminary experiments, we checked that **1** and **2** could be readily oxidized by a similar procedure. We observed by ^1H NMR the formation of the analogues of **3'**: $[(\text{Cp}^*)_2\text{Sm}(\mu\text{-Me})_2\text{AlMe}_2]_2$ (**1'**) and $[(\text{Cp}^{\text{Ph}_3})_2\text{Sm}(\mu\text{-Me})_2\text{AlMe}_2]_2$ (**2'**) [Eqs. (3) and (4), respectively]. Unfortunately, the new materials, obtained as an orange oil, did not crystallize, even at low temperature (-20°C):



Nevertheless, despite the paramagnetism of the samarium, it was possible to make a unambiguous interpretation of the NMR spectra. It has previously been shown by ^1H NMR that **3'** adopted in solution a dimeric structure, **3'a**, in equilibrium with a monomeric one, **3'b** [13]. The non-bridged Al–Me signals of the dimeric **3'a** and monomeric **3'b** were recorded at $\delta = -2.26$ and 1.63 ppm, respectively. We recorded analogous signals at $\delta = -2.11$ and 1.70 ppm for **1'**, which might be connected to the presence of both dimeric **1'a** and monomeric **1'b**, in equilibrium (Scheme 2). On the other hand, only one signal appeared in the spectrum of **2'** ($\delta = 2.3$ ppm), indicating that the monomeric **2'a** is largely predominant.

The presence of a propyl chain instead of a methyl group does not induce a dramatic change of the structure in solution. With the larger, bulky Cp^{Ph^3} ligand, the percentage of dimeric form is strongly decreased.

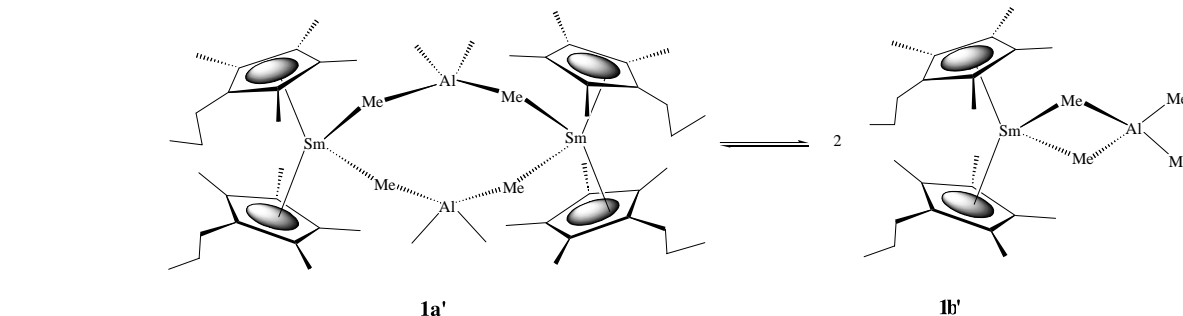
Also, as reported by Evans et al. [14], the $(\mu\text{-Et})\text{Sm}(\mu\text{-Et})$ angle of the monomeric form of $[\text{Cp}_2^*\text{Sm}(\mu\text{-Et})_2\text{AlEt}_2]$ exhibits a value of 80° [14], whereas the $(\mu\text{-Me})\text{Sm}(\mu\text{-Me})$ angle in the dimeric **3'a** is found at 85° . The value of this angle is also clearly depending on the bulkiness of the two cyclopentadienyl surrounding the opposite side of the metal: the more bulky the Cp, the smaller the $(\mu\text{-R})\text{Sm}(\mu\text{-R})$ angle. Thus, one may conclude that the preferential form for a complex bearing bulky Cp ligands would be the monomeric one, since it is the form with the lowest value of $(\mu\text{-R})\text{Sm}(\mu\text{-R})$ angle. This is in accordance with our NMR observations concerning the Cp^{Ph^3} series.

It was shown that complex **3** was able to polymerise 1,3-butadiene in the presence of aluminium cocatalysts, with a very high level of *cis*-1,4 microstructure [9]. Similarly, we studied the catalytic properties of the new complexes and Table 1 summarizes the results of the reactions performed in toluene at 50°C with the divalent samarocenes (**1**)–(**4**), in the presence of MAO.

2.3. Butadiene polymerisations with divalent samarocenes/MAO

All the samarocenes showed some activity. The highest one was obtained with complex $\text{Cp}_2^*\text{Sm}(\text{THF})$ (**1**) (72% yield in 1 h 30 min, run 1). In similar conditions, with decamethylsamarocene **3**, a yield of 40% is obtained in 20 h (run 3). This result could be explained by the presence of one additional THF molecule in **3** vs. **1**, leading to a decrease of catalytic activity.

Table 1
Polymerisation of 1,3-butadiene with samarocene/MAO in toluene^a



Scheme 2. Equilibrium between the dimer and the monomer of the bimetallic compound **1'**.

Table 1
Polymerisation of 1,3-butadiene with samarocene/MAO in toluene^a

Run	Samarocene	[BD] ₀ /[Sm]	Time (h)	Yield (%)	Microstructure ^b		
					<i>cis</i> -1,4 (%)	<i>trans</i> -1,4 (%)	1,2 (%)
1	1	1420	1 h 30 min	72	39.1	55.9	5
2	2	960	20	13	97.1	2.9	~0
3	3	1300	20	40	50.9	44.3	4.8
4	4	1480	16	10	76.2	19.5	4.3

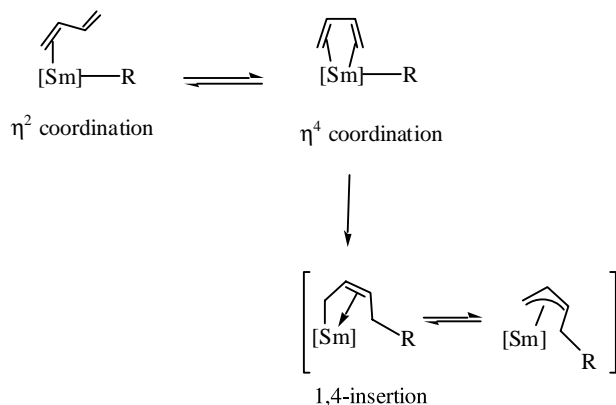
^a Polymerisation conditions: $[\text{Sm}] = 4 \times 10^{-3}$ M; $V(\text{toluene}) = 4.5$ mL for runs 1–3 and 5; 6.5 mL for run 4; $T = 50^\circ\text{C}$; $[\text{MAO}]_0/[\text{Sm}]_0 = 200$; $[\text{BD}]_0$: initial butadiene concentration.

^b Measured by ^1H and ^{13}C NMR in CDCl_3 .

When comparing the runs 1–4 it appears that the activity is higher for the more electron rich catalysts. Indeed, the better electron donation of the cyclopentadienyl ligand could be related to the facility of insertion of the monomer into the Sm active bond (Scheme 3).

In runs 1, 3 and 4, mixtures of *cis*-1,4- and *trans*-1,4-polybutadiene were obtained. This feature is in accordance with an η^4 -coordination of the monomer to the metal, followed by the *anti/syn* isomerization [15].

The result is different for run 2: with the $(\text{Cp}^{\text{Ph}_3})_2\text{Sm}(\text{THF})/\text{MAO}$ catalyst, a high *cis*-stereospecificity (97.1%) is observed. In this system, the samarium atom bears Cp ligands containing electron-withdrawing substituents, which will favour an η^4 -coordination step, bringing 4 electrons to the demanding samarium metal (Scheme 3). The η^4 -coordination is also favoured in case of low steric hindrance, and the bimetallic active species resulting from the reaction of **2** with MAO was found monomeric, instead of partly dimeric with **1** and **3** (see Section 2.2). Moreover, the activity is low (13% yield in 20 h). Thus, the crucial point in the propagation seems to be the insertion of the monomer into the active bond, rather than the coordination. In this case (run 2), the more electron-withdrawing the ligands, the easier the coordination of the monomer, but the more difficult the migration of the alkyl group (which results in the insertion into the active bond).



Scheme 3.

For the **4**/MAO catalyst, the high bulkiness of the Cp^{Ph_3} ligand could induce an η^2 -coordination but the low percentage of 1,2-polymer is characteristic of the η^4 -coordination, furthered by the absence of coordinated THF in **4**, and followed by the *anti/syn* isomerization.

2.4. Butadiene polymerisations with samarocene/MMAO

The divalent samarocenes were also tested for the polymerisation of 1,3-butadiene in the presence of MMAO. This modified methylaluminumoxane, less bridging but more bulky cocatalyst, contains both isobutyl and methyl substituents [16]. Table 2 summarizes the results of the reactions carried out with complexes **1–4** in the presence of MMAO, in toluene at 50 °C.

In the case of complex **3**, no real difference of stereospecificity can be observed between MMAO (run 7) and MAO (run 3) as cocatalyst. With complex **1**, rather than the nature of the cocatalyst, the stereospecificity appears to follow the concentration of monomer (runs 5/1/6, from 26% to 85% *cis*-1,4). Thus, the isomerisation from *anti* to *syn*, consecutive to the η^4 -coordination, is not favoured in the presence of a high proportion of monomer.

Concerning the activity, the use of MMAO rather than MAO really improves the activity of complex **3**, as reported by Wakatsuki and co-workers [9]: in similar reaction conditions, the yield increases from 40% (run 3) to 92% (run 7). The behaviour is different for complexes **1**, **2** and **4**. In the case of **1**/MMAO, the yield actually reaches 100%, although this requires significantly longer reaction times (run 5 vs. run 1). Even with an increase of the butadiene concentration (run 6), the rate of polymerisation remains quite slow. Complexes **2** and **4** are totally inactive in the same conditions (runs 8 and 9). This decrease of activity between complex **3**, and complexes **1**, **2** and **4**, can be related to the steric hindrance. The presence of the propyl chain of the Cp^{Pr} in **1**, the voluminous Cp ligands in **2** and **4**, clearly appears to be a drawback when used associated to the bulky cocatalyst MMAO.

Finally, it must be noted that the two bimetallic complexes **1'** and **2'** were tested for 1,3-butadiene poly-

Table 2
Polymerisation of 1,3-butadiene with samarocene/MMAO in toluene^a

Run	Samarocene	[BD] ₀ /[Sm]	Time (h)	Yield (%)	Microstructure ^b		
					<i>cis</i> -1,4 (%)	<i>trans</i> -1,4 (%)	1,2 (%)
5	1	680	20	100	26.2	68.9	4.9
6	1	2030	19	28	85.4	10.8	3.8
7	3	1330	15	92	56.4	40.0	3.6
8	2	900	16	–	–	–	–
9	4	1480	15	–	–	–	–

^a Polymerisation conditions: [Sm] = 4×10^{-3} M; $V(\text{toluene}) = 4.5$ mL; $T = 50$ °C; [MMAO]₀/[Sm]₀ = 200; [BD]₀: initial butadiene concentration.

^b Measured by ¹H and ¹³C NMR in CDCl₃.

merisation, alone or in presence of $\text{Al}(\text{iBu})_3/\text{HNET}_3\text{BPh}_4$, and that no polymerisation occurred.

3. Conclusion

By using quite different cyclopentadienyl ligands, Cp^{*} and Cp^{Ph_3} , we obtained the corresponding new divalent samarocenes $\text{Cp}_2^*\text{Sm}(\text{THF})$ (**1**) and $(\text{Cp}^{\text{Ph}_3})_2\text{Sm}(\text{THF})$ (**2**), both monosolvated according to NMR data and elemental analysis.

The ability of these complexes to polymerise 1,3-butadiene was evaluated in the presence of MAO or MMAO. In order to discuss the influence of the nature of the cyclopentadienyl ligands on the activity and the microstructure, $\text{Cp}_2^*\text{Sm}(\text{THF})_2$ (**3**) and $(\text{Cp}^{\text{Ph}_3})_2\text{Sm}$ (**4**), were tested in the same conditions.

Complex **1** shows the highest activity, in the presence of MAO, giving a mixture of *cis*-1,4 and *trans*-1,4-polybutadiene. At the opposite, **2**/MAO leads to up to 97% of *cis*-1,4 regular structure but with a low activity. MMAO cocatalyst is very sensitive to the steric hindrance of the samarocene it is used with: the activity decreases from **1**/MAO to **1**/MMAO system, and no activity is observed in the case of complexes **2** and **4**. Actually, MMAO appears to be suitable only in association with decamethylsamarocene **3**.

As a summary, steric hindrance of the less electron donating Cp^{Ph_3} ligands, in complex **2**, does not impede the η^4 -coordination of the monomer. To explain the slowness of the polymerisation in this case, one must exclude the *anti-syn* isomerisation, because it would lead to the formation of *trans*-polyisoprene. The determining step of the whole process is more likely the insertion, which might be disfavoured with the less electron rich metallocene **2**.

On the other hand, the reactivity of complex **4** seems to be strictly governed by steric factors, the Cp^{Ph_3} ligands hindering the coordination of the monomer.

Complexes **1** and **3** behave as efficient catalysts, their peralkyl substituted Cp ligands are good compromises for both coordination and insertion steps.

The bimetallic complexes **1'** and **2'**, obtained by treatment of **1** and **2** with AlMe_3 , were found inactive alone or in presence of $\text{Al}(\text{iBu})_3/\text{HNET}_3\text{BPh}_4$.

4. Experimental

All manipulations were carried out under argon using standard vacuum line techniques and a glove box. The solvents were dried on sodium-benzophenone ketyl and deoxygenated by distillation immediately before use. NMR spectra were recorded on Bruker Avance 300 or DRX 500 spectrometers in C_6D_6 (organometallics) or CDCl_3 (polymers) at 300 or 500 MHz, respectively.

Chemical shifts are expressed in parts per millions downfield from external TMS. Elemental analyses were performed with a Fisons EA 1108 CHON apparatus. Butadiene was dried in a solution of $\text{Cp}_2\text{TiCl}_2/\text{AlEt}_3$ in toluene. SmI_2 was purchased from Aldrich and used without purification. AlMe_3 (toluene solution, 2 M) and MAO (toluene solution, 10 wt%) were purchased from Aldrich, MMAO (heptane solution, 7% Al wt.) from Akzo Nobel. $\text{Cp}_2^*\text{Sm}(\text{THF})_2$ (**3**) [7], $(\text{Cp}^{\text{Ph}_3})_2\text{Sm}$ (**4**) [12], KCp^* [17], were synthesized as described in the literature. KCp^{Ph_3} was prepared by treatment of the corresponding diene [18] with KH in THF.

4.1. Preparation of $(\text{Cp}^*)_2\text{Sm}(\text{THF})$ (**1**)

SmI_2 (500 mg, 1.23 mmol) and KCp^* (475 mg, 2.34 mmol) were dissolved in 50 ml of THF. The dark brown solution was stirred at room temperature for 12 h. After filtration, the solvent was removed and 40 mL of toluene were added on the brown oil. Some salts were eliminated by a second filtration, the toluene was evaporated and 537 mg of a brown solid of **1** were obtained (79%). *Anal.* Calc. for $\text{C}_{28}\text{H}_{46}\text{SmO}$: C, 61.27; H, 8.38. Found: C, 62.63; H, 8.44%. NMR (C_6D_6 , 333 K): ^1H : δ 15.66 (br, 4H, THF), 8.66 (t, 3H, CH_3 (^nPr)), 6.93 (br, 4H, THF), 6.31 (s, 6H, $\text{C}_5\text{Me}_4^{\text{Pr}}$), 1.66 (br, 2H, CH_2 (^nPr)), 0.03 (s, 6H, $\text{C}_5\text{Me}_4^{\text{Pr}}$), -1.61 (br, 2H, CH_2 (^nPr)).

4.2. Preparation of $(\text{Cp}^{\text{Ph}_3})_2\text{Sm}(\text{THF})$ (**2**)

SmI_2 (250 mg, 0.62 mmol) and KCp^{Ph_3} (394 mg, 1.18 mmol) were dissolved in 40 ml of THF. The dark brown-red solution was stirred at room temperature for 12 h. After filtration, the solvent was removed and the brown oily residue was extracted with 30 mL of toluene. The toluene was slowly evaporated to dryness, leaving 315 mg of a black-brown solid of **2** (63%). *Anal.* Calc. for $\text{C}_{50}\text{H}_{42}\text{SmO}$: C, 74.21; H, 5.23. Found: C, 73.97; H, 5.14%. NMR (C_6D_6 , 298 K): ^1H : δ 12.11 (br, 4H, THF), 11.41 (br, 2H, $\text{C}_5\text{H}_2\text{Ph}_3$), 10.90 (br, 2H, m' -), 10.68 (br, 4H, o -), 10.05 (br, 2H, o' -), 8.95 (br, 4H, m -), 8.58 (t, 1H, p' -), 7.66 (t, 2H, p -), 1.98 (br, 4H, THF) (o -, m -, p - are relative to the 2 equivalent phenyl groups and o' -, p' -, m' - to the third non-equivalent to the others).

4.3. Oxidation reaction of **1** and **2**

An excess of AlMe_3 (toluene solution 5.47 mL, 10.9 mmol) was slowly added at ambient temperature to a brown solution of $(\text{Cp}^*)_2\text{Sm}(\text{THF})$ (**1**) (182 mg, 0.30 mmol) in 30 mL of toluene. The reaction was stirred at room temperature for 24 h. A red-orange solution was obtained and a blackish, metal-like precipitate deposited. The mixture was filtered and the precipitate was washed once with toluene. The solvent was evaporated to dryness and a deep orange oil (112 mg, 66%) was

obtained. NMR analysis was consistent with the formation of $[(Cp^{*'})_2Sm(\mu Me)_2AlMe_2]_2$ (**1'**): (C_6D_6 , 298 K): 1H : δ 3.09 (q, 2H, $CH_2(^nPr)$), 2.18 (q, 2H, $CH_2(^nPr)$), 1.94 (t, 2H, $CH_2(^nPr)$), 1.8 (t, 3H, $CH_3(^nPr)$), 1.70 (br, 3H, $(\mu Me)_2AlMe_2$ **1b'**), 1.57 (t, 2H, $CH_2(^nPr)$), 1.34 (t, 3H, $CH_3(^nPr)$), 0.90, 0.74, 0.68, 0.72 (s, 6H, C_5Me_4Pr each), -2.11 (s, 3H, $(\mu Me)_2AlMe_2$ **1a'**), -14.22 (br, 3H, $(\mu Me)_2AlMe_2$ **1a'**), -17.41 (br, 3H, $(\mu Me)_2AlMe_2$ **1b'**).

Following the same procedure, from $(Cp^{Ph_3})_2Sm(THF)_2$ (**2**) (200 mg, 0.247 mmol) and an excess of $AlMe_3$ (7.4 mL, 14.8 mmol) in 15 mL of toluene, an orange oil (125 mg, 61%) was obtained, which did not become solid even after a prolonged evaporation. NMR analysis was consistent with the formation of $(Cp^{Ph_3})_2Sm(\mu Me)_2AlMe_2$ (**2'**): (C_6D_6 , 298 K): 1H : δ 15.57 (s, 2H, $C_5H_2Ph_3$), 6.65 (t, 2H, *p*-), 6.35 (t, 4H, *m*-), 6.07 (t, 1H, *p'*-), 5.97 (d, 4H, *o*-), 5.91–5.81 (overlapped signals, 2H, 2H, *o'*-, *m'*-), 2.3 (br, 3H, $(\mu Me)_2AlMe_2$), -15.5 (br, 3H, $(\mu Me)_2AlMe_2$).

4.4. Butadiene polymerisation

In a typical procedure (run 1, Table 1), 10 mg of **1** (1.77×10^{-2} mmol), 2.04 g of MAO (10 wt% in toluene, 3.5 mmol) and 2 mL of toluene, were mixed in a 500 mL flask, inside a glove box. The flask was connected to the vacuum line and the butadiene condensed directly under vacuum. The quantity of butadiene in the flask was determined by weighting it. The flask was put at 50 °C for 15 h under stirring (the reaction could be finished earlier than, depending on the viscosity of the medium). At the end of the reaction, the flask content was dissolved in toluene with bis-*tert*-butylphenol as stabilizing agent. The resulting solution was poured into ethanol to precipitate the polymer, which was isolated and dried under vacuum.

4.5. Polymers analyses

The microstructure of the polybutadienes was determined by 1H and ^{13}C NMR spectroscopy in $CDCl_3$. 1H :

δ 4.8–5.2 ($=CH_2$ of 1,2-butadiene unit), 5.2–5.8 ($-CH=$ of 1,4-butadiene unit and $-CH=$ of 1,2-butadiene unit). $^{13}C\{^1H\}$: 27.4 (1,4-*cis*-polybutadiene), 32.7 (1,4-*trans*-polybutadiene), 127.7–131.8 (1,4-polybutadiene unit) and 113.8–114.8 and 143.3–144.7 (1,2-polybutadiene unit).

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