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Non-hindered ansasamarocenes, versatile catalysts for diene/olefin/polar monomer copolymerisations. What is really the active species?

Denise Barbier-Baudry [a,*], Fanny Bonnet [a], Bruno Domenichini [b], Alain Dormond [a], Marc Visseaux [a]

[a] *Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, Faculté des Sciences Mirande, LSEO, UMR 5632, Université de Bourgogne, 9 Avenue Alain Savary, BP 47870, 21078 Dijon Cedex, France*

[b] *Laboratoire de Recherche sur la Réactivité des Solides, Faculté des Sciences Mirande, LRRS, UMR 5622, Université de Bourgogne, 9 Avenue Alain Savary, BP 47870, 21078 Dijon Cedex, France*

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Abstract

Catalytic systems containing an ansabiscyclopentadienyllanthanide core and lithium and/or magnesium salts are obtained by reaction of the chloride precursors with allyllithium. These allyl complexes lead to the same active species which polymerises 1,3-dienes, copolymerises 1,3-dienes and α-olefin or α,ω-dienes or allows the controlled diblock polyisoprene/polycaprolactone copolymerisation. The exact nature of this active species and of the allyl precursors is investigated here. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lanthanide; Samarium; Allyl complexes; Diene; Olefin; Polymerisation; Copolymerisation

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1. Introduction

Homogeneous single site catalysts for olefin polymerisation have developed rapidly over the last 10 years. Nevertheless, until now, only a few systems can perform the diene/olefin copolymerisation [1]. These copolymers could be materials of industrial importance but their synthesis remains a challenging problem because usually, the dienes, better ligands, are a poison for the olefin polymerisation catalysts. The search of new catalytic systems to achieve this goal is within the scope of organometallic chemistry.

The lanthanide derivatives nowadays attract much attention because rare earths do not present the toxicity of the heavy metals and are therefore environmentally friendly. Allyllanthanide complexes were found efficient initiators for the diene homopolymerisation [2] whereas metallocenic lanthanide alkyl or hydride complexes were found efficient for the olefins' polymerisation without any addition of a co-catalyst [3]. The sterically demanding C_5Me_5 ligand led to a complete series of complexes which were largely investigated [4], but if these compounds are active in the olefin polymerisation, they were found inactive towards the dienes. In the latter case, the insertion of the diene lead to an allylic complex, which is stable towards the further diene insertion [5]. Steric hindrance could also be invoked, and the use of less hindered complexes [6] might make the coordination and the further insertion of a second molecule of diene easier. Two metallocenic systems with monosubstituted cyclopentadienyl ligands were recently described: a neodymium complex, obtained in situ by the addition of a $BuLi–{}^iBu_2AlH$ mixture to $(CMe_3C_5H_4NdCl)_2$ was found active in the butadiene/ethylene copolymerisation [7] and a few years ago we had obtained the first lanthanide system allowing the copolymerisation of a diene and terminal olefins [8]. This catalyst was also able to copolymerise isoprene with α,ω-dienes, leading to functionalisable polymers [9]. The first analytical data of the catalyst spoke in favour of the formation of an anionic bisallylic complex $(CMe_2C_5H_4)_2Sm(allyl)_2Li(DME)$ [10]. However, some aspects of the reactivity were unclear: the nature of the

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* Corresponding author. Tel./fax: +33-3-8039-6084.

E-mail address: baudryd@u-bourgogne.fr (D. Barbier-Baudry).

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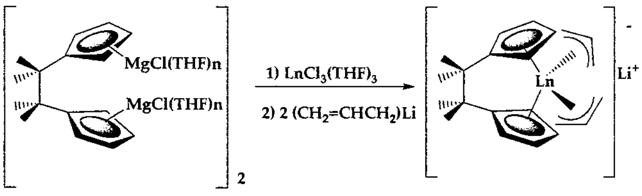
formed polymers (nearly pure *trans* PI and low polydispersity indexes) denoted the presence of a single site active species, and implied the non-intervention of the allyllithium in the polymerisation, which should lead to a mixture of *cis* and *trans* PI. The hypothesis that the allyllithium would only act as a protecting group of the active species being not supported by any strong arguments, it appeared necessary to come back to the real nature of the catalyst precursor. We present here a detailed study of the catalytic systems obtained by reactions of allyllithium with ansametallocene derivatives, $[(CMe_2C_5H_4)_2SmCl(THF)]_2$ and $[(CMe_2C_5H_4)_2SmClMgCl_2(THF)_3]_2$.

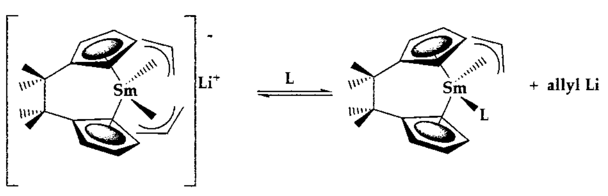
2. Syntheses

2.1. Historical background

The neutral complex $[(CMe_2C_5H_4)_2Sm(allyl)]_n$ had been found inactive in the isoprene polymerisation. A diene, unlike THF or nucleophilic carbenes, does not possess a strong ligand ability and is unable to dissociate the polynuclear samarium complex. On the opposite, the anionic complex $[(CMe_3C_5H_4)_2SmMe_2]Li$ was fairly active in ethylene polymerisation, the dissociation of the MeLi moiety leading to a neutral active species [10]. The system was active only within a very short period of time, the rapid loss of activity could be due to the fast rearrangement into inactive triscyclopentadienyl derivative. To prevent the disproportionation of non-hindered biscyclopentadienyl derivatives, bridged ligands can be used. The dianion $[CMe_2C_5H_4\text{-}CMe_2C_5H_4]^{2-}$ which is the chelating analogue of a pair of $(CMe_3C_5H_4)^-$ anions is obtainable by the reductive dimerisation of fulvene [11] and allows the access to metallocenes derivatives. We intended to synthesise anionic allylic derivatives, the first catalytic systems were made from neodymium complexes: the natural abundance of this element, the greater size of the neodymium ion allowing a better access of the monomer to the metal, make this element especially convenient for catalytic purposes. Nevertheless, for studies in solutions implying NMR investigations, samarium complexes are more convenient, NMR spectra of the complexes — in the absence of fluxional behaviour — are usually well resolved and easily interpreted.



Scheme 1. The target molecules.



Scheme 2. The dynamic exchange process.

The target molecules were anionic complexes $[(CMe_2C_5H_4)_2Ln(allyl)_2]Li$ (Ln = Nd or Sm) (Scheme 1).

Active initiators towards isoprene [10] or styrene [12] polymerisations were obtained by addition of two equivalents of allylLi on a crude material formed by mixing the lanthanide chlorides $LnCl_3(THF)_3$ (Nd, Sm) with the magnesium reagent $[(CMe_2C_5H_4)_2MgCl_2(THF)_3]_2$. Both compounds were insoluble in C_6D_6, and only sparingly soluble in the presence of a tenfold excess of oxygenated ligand, THF or dioxane. At room temperature, the NMR spectrum of the samarium derivative showed the signals of the ansa ligand only, while at 70 °C, a two allyl signal pattern (integrated in the ratio 2H/8H) revealing a dynamic exchange process (Scheme 2) was observed.

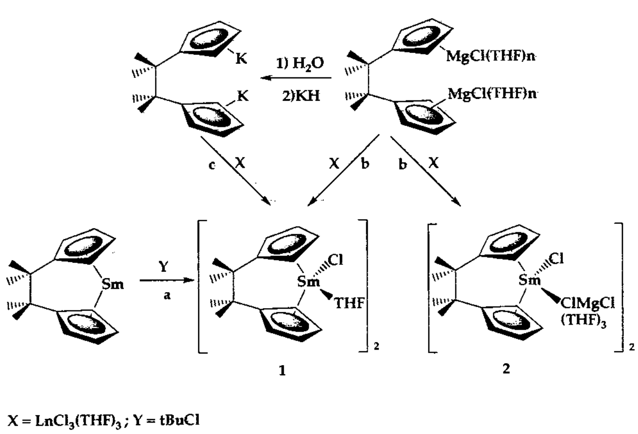
From the crude samarium derivative, after crystallisation, a microcrystalline brick-red powder and a small crop of well formed (but too thin for a crystal structure determination) red crystals could be collected. The elemental analysis of the crystals was compatible with the formula $[(CMe_2C_5H_4)_2Sm(allyl)_2]Li(DME)$ However the NMR spectrum of the powder, recorded in deuterated THF, showed the presence of only one paramagnetic allyl ligand. The above reported formula was therefore not representative of the major part of the material. Moreover, the analogous neodymium complex contained magnesium in a nearly 1:1 Mg/Nd ratio. The synthetic methods were systematically revised in the samarium series.

2.2. Synthesis of the chlorides

Two samarium chlorides were described, $[(CMe_2C_5H_4)_2SmCl(THF)]_2$ (**1**) [13] and $[(CMe_2C_5H_4)_2SmClMgCl_2(THF_3)]_2$ (**2**) [14].

Two syntheses of **1** were published (Scheme 3), the first one used the samarium metal to promote dimethylfulvene coupling, followed by the subsequent oxidation of the ansasamarium^{II} compound with ^{t}butylchloride (method a) [13a,b]. The second one used the magnesium reagent $(CMe_2C_5H_4MgCl)_2(THF)_4$ (method b) [13c].

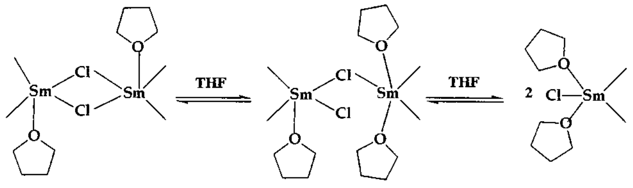
Following method a, the yields were low and the purity of the crude products (NMR control) was not



Scheme 3. Syntheses of complexes **1** and **2**.

Table 1
^{1}H-NMR data for ansasamarium chloro derivatives **1** and **2**

Compound	C_5H_4	Me	THF
1	14.80; 7.47	1.42	2.72; 0.9
1+10THF	13.19; 7.66	1.24	2.92; 1.05
2	15.5; 8.11	1.53	3.80; 1.39



Scheme 4. Opening of the dimer bridge.

satisfactory. The course of the reaction was greatly influenced by the nature of the metal powder. The commercial samples of samarium powder especially did not lead to reproducible experiments.

In a precedent work [10], we wrote that the crude material obtained following method b was not yellow, but orange. On the basis of the NMR integration, it was estimated that this crude material was essentially the known samarium–magnesium compound **2** [14]. It was not possible to eliminate the magnesium chloride ligand by crystallisation or by extraction with non-polar solvents. It has been also observed that handling of the mixture was not recommended: after the usual work up, a less pure material was recovered (numerous new signals and high broadening of the CpH signals in the NMR spectrum).

We obtained **1** by using the potassium salt of the chelating dianion $(CMe_2C_5H_4)_2^{2-}$ (see Section 7) instead of the magnesium reagent (method c). After crystallisation, a correct elemental analysis was obtained. A suitable crystal was submitted to X ray analysis, the unit cell was found identical to that previously published [13c]. One points out that the well crystallised, pure complex **1** is only sparingly soluble in C_6D_6. The dissolution of 5 mg of **1** is not complete in 0.5 ml of C_6D_6, and it is remarkable that the THF signals integrate for two THF molecules per samarium whereas the pure complex contains only one molecule of THF. A similar behaviour has been observed for cyclooctatetraenyl complexes [15].

After some months of storage at room temperature in the glove box (argon, less that 2 ppm O_2), a strong decreasing of the solubility of **1** in benzene was observed: by using the standard amounts (5 mg, 0.5 ml), a major part remained undissolved, the recorded spectrum corresponded to a very dilute solution of **1**. The solution was taken out and a second amount of C_6D_6 was added, the solid did not dissolve, only traces of **1** could be detected in the spectrum.

When the synthesis of **1** is performed at 80–90 °C, a temperature allowing the removal of THF, the crude product is quite insoluble in toluene and the colour is slightly different, rather beige than yellow. The addition of at least 3THF per samarium is necessary to obtain a solution. The alkylation of this crude product with a hexane solution of butyllithium does not lead to a well defined compound and a triscyclopentadienyl complex is formed (see Scheme 5). It is assumed that this crude product has not the known dimeric structure, but as a consequence of the loss of THF, possesses a higher polynuclearity. In this associated form, in the presence of an anionic reagent, the ligand redistribution occurs easily. The NMR spectra of the two complexes **1** and **2** are similar (Table 1).

The Cp signals are recorded in the range observed for analogous Cp′ complexes (Cp′ = $CMe_3C_5H_4$) [16]. The addition of THF to a solution of **1** (one to ten equivalents) induces a slight modification of the chemical shifts (see Table 1): the chemical shifts difference of the Cp signals decreases and the methyl signal is shifted to a higher field. This evolution is probably due to an equilibrium with the monomeric $(CMe_2C_5H_4)_2SmCl(THF)_n$ units, after opening of the dichloro bridge (Scheme 4).

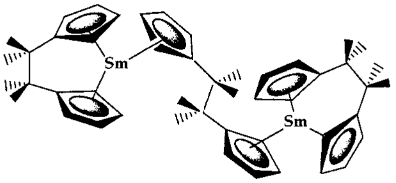
In the same way, it has been precedently observed [16] that the Cp signals of $[(CMe_3C_5H_4)_2SmCl]_2$, $\delta = 17.5$ and 12.3 ppm in benzene solution, shift to a very close position, $\delta = 10.5$ and 10.4 ppm, in deuterated THF solution. It is noteworthy that a confusion occurred in the attribution of the Cp and THF signals in the referenced paper [13a]. The increase in the intensity of the signals at $\delta = 2.72$ and 0.9 after addition of THF establishes their attribution unambiguously.

Before the bulk syntheses, experiments were performed at NMR scale. After heating in C_6D_6 (from time to time the mixture was stirred by sonication), a stoichiometric mixture of $SmCl_3(THF)_3$ and $(CMe_2C_5H_4K)_2$, the spectra were recorded. After 1.5 h, the reaction was complete and a unique set of signals corresponding to **1** (and two additional THF molecules) was obtained. However, before the end of the reaction (30 min–1 h), another set of signals: two C_5H_4 patterns and two CMe_2 signals in a ratio 2:1 was also present. This set of signals was the only one obtained when the same experiments were conducted with 1.5 equivalents of $(CMe_2C_5H_4K)_2$, indicating the probable formation of a di-(or polynuclear) $[(CMe_2C_5H_4)_2]_3Sm_2$ compound (Scheme 5).

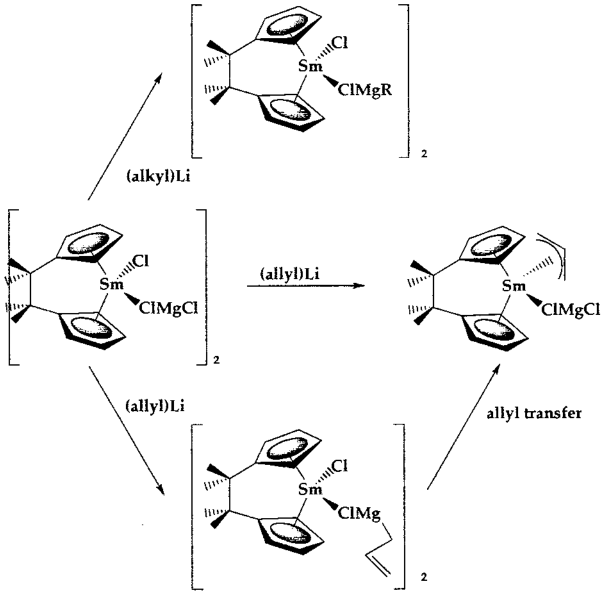
2.3. Access to the catalysts

2.3.1. Choice of the best precursor for the syntheses

Both complexes **1** and **2** were tested as starting materials to synthesise polymerisation initiators. It was important to establish if it was essential to use **1** because its synthesis requires indeed a long route: after the synthesis of the common magnesium reagent, three additional steps (hydrolysis, distillation, metallation by potassium) are necessary. Preliminary experiments at NMR scale showed that after addition of allylLi (dioxane adduct) to a solution of **1** or **2**, paramagnetic allyl signals appeared in the same range. It was clear that using **2** as precursor, the allyl group was finally coordinated to the samarium ($\delta = 9.52$, 8.61, 7.06 ppm) (Scheme 6).



Scheme 5. The ansatriscyclopentadienyl species (THF are omitted).



Scheme 6. Alkylation vs. allylation of complex **2**.

The easy obtention of samarium allyl derivative from **2** led to carrying out the bulk syntheses from this precursor, affording two different species named **A** and **B**. Nevertheless according to the encountered difficulties in understanding the role of the magnesium moiety remaining present in these catalysts, the allylation of **1** was also performed, leading to **C**. The bulk syntheses were conducted in toluene solution to facilitate the salts eliminations.

2.3.2. Catalysts A and B

For the syntheses from **2**, the use of two equivalents of allylLi was found necessary to obtain the total consumption of **2** within a few hours. In the presence of only one equivalent of the reagent, after 48 h, the reaction remained incomplete.

In a first step, **2** is obtained (as described above) by mixing the stoichiometric quantity of $SmCl_3(THF)_3$ and $[(CMe_2C_5H_4)MgCl(THF)_2]_2$, the orange toluene solution is then filtered and poured on the solid allylLi-(dioxane), leading to a red solution and off-white salts, eliminated by filtration. This crude solution was treated in two different ways, leading to **A** or **B.**

Way 1. The reddish toluene mixture containing two different ethers, THF and dioxane, provided by the reagents, was pumped off, then dimethoxyethane (DME) was added affording a deep-red solution. This solution was evaporated and diethylether was condensed onto the expanded oil, leading to a pale orange solution and a red brown precipitate. The precipitate (**A**) was isolated, washed with diethylether and dried. It was not soluble in C_6D_6, therefore the NMR spectrum was recorded in deuterated THF: the signals of chelating DME were present, at the diamagnetic place (THF usually can displace this chelating, but weaker ligand). The paramagnetic signals corresponded to a $(CMe_2C_5H_4)_2Sm(allyl)$ moiety, some diamagnetic olefinic impurities were also present. The formula $(CMe_2C_5H_4)_2Sm(allyl)(DME)$ could be proposed, but it did not account satisfactorily for the insolubility of such a molecular, neutral complex. The formation of an anionic complex would imply the incorporation of a lithium cation to ensure the global neutrality. To conclude on the presence of a second metal, XPS analyses were performed (vide infra).

In another synthesis, the expanded oil was dissolved in a small volume of DME and the addition of diethylether led to a microcrystalline brick-red powder (**A**′). The yield was lower (30% instead of 78%).

Way 2. The crude mixture was obtained the same way and after removal of the toluene, crystallisation attempts were made in dioxane. Those were unsuccessful and the mixture was pumped dry, then dissolved in a small volume of THF. As precedently, the evaporation led to an expanded solid, and a powder was finally obtained after treatment with diethylether. This com-

Table 2
^{1}H-NMR data for catalysts **A**–**C**

Catalyst; solvent	C_5H_4	Me (12H)	DME (**A**); THF (**B**)	Allyl (CH_2=CH–CH_2–)
A or **A′**; C_4D_8O	7.94 (4H); 5.77 (4H)	1.70	3.35 (4H); 3.19 (6H)	9.53 (1H); 8.6 (2H, broad);7.1 (2H, broad)
B; C_6D_6	8.0 (4H, broad); 6.06 (4H)	1.53	2.68 (12H);0.89 (12H)	10.2 (1H, broad); 8.88 (2H);7.5 (2H, broad)
C; C_6D_6, THF	8.09 (4H, broad); 5.97(4H)	1.90	–	10.15 (1H, broad); 8.90 (2H);7.50 (2H)

pound was fairly soluble in C_6D_6, the signals integration allowed to propose the formula $(CMe_2C_5H_4)_2Sm(allyl)(THF)_3$ for **B**.

2.3.3. Catalyst *C*

From **1** and only one equivalent of allylLi(dioxane), a yellow complex (**C**), turning red (**C′**) in the presence of THF vapour was formed. The yellow form was not soluble in benzene, the red adduct showed a spectrum almost identical to that of compound **B**. However, **B** and **C** were not considered as identical because **B** could not be desolvated. NMR data of catalysts **A**–**C** are reported in Table 2.

2.3.4. XPS analyses of the catalysts

Catalyst **C** was less attractive than the other two: the synthesis was longer and it could not be conserved without a strong decreasing of its activity: further use was thus not envisaged. Consequently only catalysts **A**, **A′** and **B** were submitted to XPS analysis. X-ray photoelectron spectroscopy (XPS) enabled us to estimate the Li, Mg and Sm ratios. XPS is well known as a technique of surface analysis, however it is possible to scan several atomic layers. Moreover, after calcination (under air, 10 h, 600–900 °C) the material can be considered as homogeneous and the content of the external shell as equivalent to the bulk one. The C, H, N, Cl elements are removed, the metals are present as oxides.

A broad scan survey was performed on each sample, in order to check the lack of contamination of the surface. The spectrum showed the presence of O, Mg, Sm and Li only, however, a very small peak due to a carbon surface pollution could be detected. The quantifications were carried out from Li1s (55 eV) and for the other elements, from the $Sm3d_{5/2}$ (1083 eV) and Mg1s (1305 eV) or from the Sm4d and Mg2s peaks, with identical results. This confirms that the surface and the bulk content are identical. The peak areas were corrected by sensitivity factors [17], the final accuracy is of about 15%.

A and **A′** samples, contained lithium whereas no lithium was found in **B**. Besides, a difference of reactivity between **A** and **B** was noted: the two samples **A** and **A′** reacted violently to air exposure, as do, for example, the RLi reagents, whereas **B** did not.

The three samples contained magnesium, nearly one Mg per Sm for **B** and **A′** and two Mg for **A**. This difference was probably due to the practical work up: **A′** was obtained in lower yield, after a crystallisation step, **A** was obtained after ether addition on a solid expanded oil. Considering the well known difficulty in eliminating magnesium salts in organic media, it could be admitted that the catalysts **A**, **A′** and **B** were contaminated by a variable quantity of non-eliminated magnesium chloride. The quantity of magnesium present, at least one per samarium, speaks in favour of the maintenance of $MgCl_2$ as ligand in the molecule, as in the starting material $[(CMe_2C_5H_4)_2SmClMgCl_2(THF)_3]_2$.

3. Catalytic experiments

3.1. Isoprene polymerisation, or isoprene/α-olefin copolymerisation

It was of great importance to test the organometallic compounds **A**–**C** in polymerisation experiments, to determine the most efficient and/or stereoselective catalyst. For this purpose, in the glove box 10 mg of **A**, **B** or **C** were weighed and put into the polymerisation flask, the monomer and comonomer added onto it. The flask was connected to a vacuum line and in some cases a solvent, usually toluene, was transferred. The mixture was magnetically stirred at 50 °C, either for a given time or until it became highly viscous. **A** or **B** dissolved readily within 5–10 min whereas **C** was not immediately soluble in the polymerisation mixture, it dissolved after a few hours. With **B** and **C** the viscosity of the medium was observed after a longer time than for **A**. In all cases, an orange–tan colour developed in the medium.

Although the course of the reactions involving catalysts **A**–**C** were slightly different, especially as for the reaction time, it was not possible to find any difference for the polymers, whatever the precursor. The polymeric materials were identical, they exhibited the same NMR spectra and the same thermo-mechanical properties (glass transition temperature, Young modulus, ...) [18].

It was observed that after 3 months storage, at ambient temperature in the glove box, **C** did not keep its catalytic activity, whereas **B** was still active after the same period. The activity of **A** was preserved after up to 2 years storage.

3.2. *A*, *a versatile catalyst*, *access to new materials*

A, easily synthesised and stable for years appeared the most convenient for further investigations. It allows in fact the copolymerisation of isoprene with hex-1-ene and longer α-olefins (C_8–C_{18}) or α,ω-dienes. In the same manner, **A** also polymerises buta-1,3-diene and copolymerises butadiene and α-olefins.

The insertion of a long alkyl chain confers elastomeric or adhesive properties to the copolymers [8b] (*trans*-polyisoprene is a brittle material), the insertion of α,ω-diene leads to the copolymers bearing a pendant vinyl group and allows further modification by grafting oxygenated hydrophilic motives on these lipophilic chains [9].

Moreover, **A** is also a good catalyst for ε-caprolactone polymerisation, thus it is possible to perform the controlled diblock polymerisation of isoprene (or isoprene/olefin copolymers) and ε-caprolactone which allows an entry in the compatibilisers materials. Some typical copolymers' data are reported in Table 3.

4. Obtention of alkyls from 1 and 2

4.1. *Syntheses*

Because there is also current interest for olefin polymerisation catalysts, some preliminary experiments concerning the alkylation of **1** and **2** were made. In particular, anionic ansasamarium alkyls $[(CMe_2C_5H_4)_2]SmR_2]Li$ would be the chelate analogues of the known complex $[(CMe_3C_5H_4)_2SmMe_2]Li$, efficient for the ethylene polymerisation [10].

Syntheses were first performed in a NMR tube, by addition of the stoichiometric quantity of the RLi reagents, R = Me, ^{n}Bu, CH_2SiMe_3, $CHSi(Me_3)_2$, on a C_6D_6 solution of **1** or **2**. In all cases well resolved spectra were obtained, the ^{1}H-NMR data of the alkyl complexes and, for comparison, those of some homologous Cp′ compounds (Cp′ = $CMe_3C_5H_4$), are reported in Table 4.

The spectra of the alkyls obtained from **1** were quite different from those obtained from **2**, only the former showed the characteristic paramagnetic signals of Sm–R moieties, the latter could be interpreted by the formation of Mg–R derivatives (Scheme 6, see below

Table 3
Characteristic data for some typical copolymers

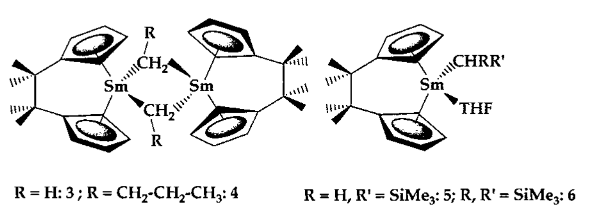
Material	Insertion %	$M_n \times 10^{-3}$ (PDI)	T_g (°C)	T_m (°C)	ΔH_m (J g^{-1})
PI [a]	–	50 (1.32)	−65	46	60
PI/hexene	11.4	33 (1.58)	−66.3	38.3	3.5
PI/decene	6	40 (1.84)	−75	36	1.6
PI/octadiene	6.5	50 (1.80)	−69	–[b]	–[b]
PI/octadiene/hexene [c]	4, 4.8	41.4 (2.0)	−66	34.5	1.2
PI/PCL [d] diblock	62 (PI) [e] 38 (PCL) [e]	50 (19)	−64.9 (PI)	35 (PI) 58 (PCL)	9 (PI) 34.5 (PCL)

[a] PI = *trans*-polyisoprene.
[b] No crystallinity, adhesive material.
[c] Terpolymer.
[d] PCl = polycaprolactone.
[e] mol%.

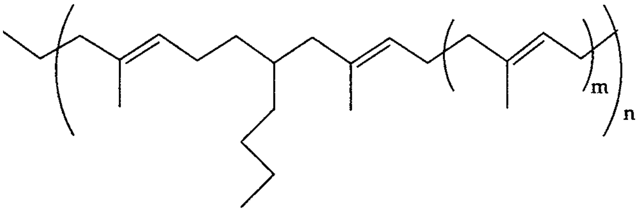
Table 4
^{1}H-NMR data for dimeric, monomeric and anionic alkyl complex obtained from **1** and **2** and Cp′ analogues **11**–**13** (C_6D_6, 297 K)

Compound	Cp	Me	THF	Alkyls
[ansaSmMe(THF)]$_2$ (**3**)	13.5; 7.46	3.02	3.2; 1.4	−26.8
[Cp′Sm(Me)]$_2$ [a] (**11**)				−26.1
[ansaSmBu(THF)]$_2$ (**4**)	10.58; 8.30	3.00	3.3; 1.4	−29.7; −16.10; −4.08; −2.7(Me)
ansaSmCH$_2$SiMe$_3$(THF) (**5**)	11.07;6.80	1.79	−1.36; −1.79	11.32 (CH$_2$) 0.25 (SiMe$_3$)
ansaSmCH(SiMe$_3$)$_2$(THF) (**6**)	11.85; 6.5	1.82	−0.46; −0.6	11.40 (CH) −0.08 (SiMe$_3$)$_2$
Cp′Sm(Me)(THF)$_n$ [a] (**12**)	7.84; 7.63	0.62		6.43
[ansaSmMe$_2$]Li(THF)$_3$ (**7**)	6.84; 6.41	3.18	4.08; 1.60	−5.06
[ansaSmBu$_2$]Li(THF)$_n$ (**8**)	7.55; 4.83	3.31	1.7; 0.23	−6.69 (4H); −0.18(8H); 4.60(3H)
[Cp′SmMe$_2$]Li(diox) [b] (**13**)	9.77; 9.07		4.15	−5.12
2 + Li[CH(SiMe$_3$)$_2$] (**9**)	13.64; 7.71	1.07	2.98; 1.06	−2.42 (CH) 0.18 (SiMe$_3$)$_2$
2 + Li(CH$_2$SiMe$_3$) (**10**)	13.50; 7.64	1.15	3.02; 1.00	−1.31 (CH$_2$, 4H) 0.43 (SiMe$_3$)

[a] Cp′ = $CMe_3C_5H_4$.
[b] diox = dioxane.



Scheme 7. Alkylation of complex **1**, monomeric or dimeric species.



Scheme 8. The structure of the isoprene/hex-1-ene copolymer.

NMR discussion). Unexpectedly, heating in refluxing benzene did not allow the transfer of the alkyl group onto the samarium atom. If an excess, two to four equivalents, of RLi was added, we only observed the increase and slight shifting of the MgCH signal, denoting an exchange of the R moiety between the Li and Mg atoms.

The ^{n}butyl derivatives were poorly stable: the NMR spectrum of a mixture of $[(CMe_2C_5H_4)_2]Sm(butyl)$ and $[(CMe_2C_5H_4)_2]Sm(butyl)_2]Li$ was observed. After 2 h, almost all the sample was precipitated, the signals last observed were those of the neutral complex, without any change of chemical shifts. At this time olefinic signals were present, denoting the loss of the butyl chain by β-H elimination.

When R is bulky (CH_2SiMe_3 and $CH(SiMe_3)_2$) the new samarium alkyls were fairly stable: in benzene solution, no decomposition was observed within a 1 or 2 days period and bulk syntheses of these alkyls were performed in toluene from **1** or from the borohydride analogue. The BH_4 ligand possesses a higher electron donating ability, the borohydrides can be isolated as monomers while the chlorides are associated, or contain supplementary ancillary ligands [19]. Therefore the BH_4 ligand can behave as a better leaving group and its substitution can occur more easily than that of the chloride.

The crude alkyl products were analysed by NMR before purification. Surprisingly, these compounds were of poor quality compared to those obtained at the NMR scale. The known alkyl signals were present, but enlarged, not well resolved and accompanied by unidentified signals. A set of signals was related to the presence of a triscyclopentadienyl compound (Scheme 5, vide supra). It is clear that for catalytic purpose, the alkylation must be done directly in the polymerisation flask.

4.2. NMR data

For the mixed samarium–magnesium complexes $[(CMe_2C_5H_4)_2Sm(L)Cl]_2$, L = $ClMgX(THF)_n$; X = Cl or R, the chemical shifts of the ansa ligand signals are nearly the same and very close to those observed for $[(CMe_2C_5H_4)_2Sm(THF)Cl]_2$ in the presence of an excess of THF. The monomeric or dimeric structure of the alkyl complexes (Scheme 7) was established by ^{1}H-NMR (Table 4).

The paramagnetic shifts of the Sm–Me (or Sm–CH_2– for the butyl derivative) of **3**, **4** or **11** are clearly related to the structure of these complexes. The presence of alkyl bridges in dimers is denoted by a strong high field shift: the $SmC\mathit{H}_2(R)Sm$ signals are observed in the -25 to -30 ppm range, whereas the terminal $SmC\mathit{H}_2(R)$ signal of a monomeric species such as **12** is downfield shifted (6.4 ppm). In the Cp′ series [10], for monomeric, non-bridged complexes, signals at $\delta = 18.5$ and 10.4 ppm were recorded for the $SmC\mathit{H}(SiMe_3)_2$ and $SmC\mathit{H}_2SiMe_3$ protons, respectively. In the same way, the chemical shifts of the ansa$SmC\mathit{H}_2SiMe_3$ (**5**), or $C\mathit{H}(SiMe_3)_2$ (**6**), are observed at low field in the range 11–12 ppm, those are therefore likely monomeric complexes too. The unbridged complexes **5** and **6** containing only one coordinated THF appear under-coordinated, but a stabilisation by agostic interaction might be involved, these interaction can play a significant role, for example, in the stabilisation of the reactive species in catalytic reactions [20].

For complexes **9**, **10**, if the signals of the Cp protons and of the ansa CH_3 protons are in the same range as for **5** or **6**, the signals of the CH_2 or CH alkyl protons are very differently shifted: + 11 ppm for **5** and **6** in which the alkyl group is directly bonded to the samarium, ca. 2 ppm for **9** and **10** in which the alkyl group is bonded to the magnesium atom. It is also noteworthy that the Sm–CH signals of the monomeric dialkyl anionic complexes **7**, **8** and **13** appear at an intermediate shift: -5, -7 ppm.

5. Discussion and general comments

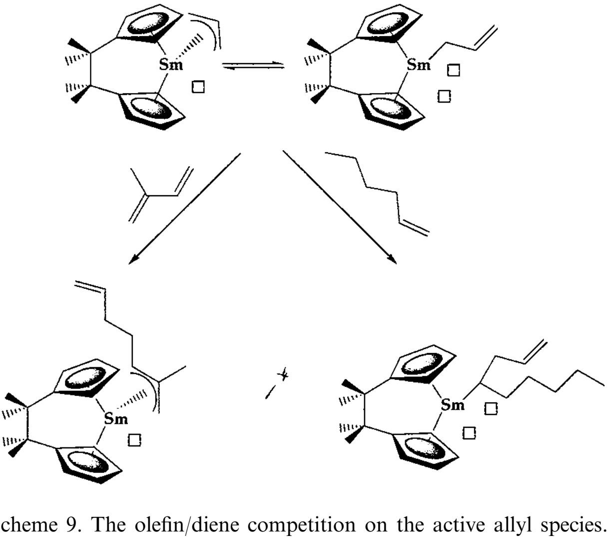
5.1. The active species and the diene/olefin competition

The three catalysts **A**–**C** led to the same original new materials, polyisoprene/α-olefins copolymers (Scheme 8). There is at the moment no other catalytic system which can generate such copolymers. The low polydispersity indexes (PDI) are typical of living single site catalysts.

Obviously, the three different catalysts lead to the same active species. This common active species cannot contain a $MgCl_2$ ligand, because **C** prepared from a potassium reagent was free of magnesium. In the polymerisation medium, the three catalysts would lead to the $(CMe_2C_5H_4)_2Sm(allyl)$ moiety. It is assumed that in this species, for the σ-allyl form, a maximum of two vacant sites (allowing the η4-coordination of the diene) may be available. Compared to the well known C_5Me_5 ligand, the chelating $(CMe_2C_5H_4)_2$ ligand is neither highly sterically demanding nor highly electron donating. As a consequence, the complexes bearing the $(CMe_2C_5H_4)_2$ ligand are penta-coordinated, see for example the crystal structures of the chlorides $[(CMe_2C_5H_4)_2SmCl(THF)]_2$ (**1**) and $[(CMe_2C_5H_4)_2SmClMgCl_2(THF)_3]_2$ (**2**) [13c,14]. In these complexes, the samarium centre is surrounded by five ligands, while only four ligands are present in the non-chelate analogue of **1**, $[(CMe_3C_5H_4)_2SmCl]_2$ [21], according to the larger steric hindrance resulting from the free rotation of the cyclopentadienyl rings. In solution, in the presence of only weak ligands, as dienes or olefins, a coordination number higher than in the solid state is not expected. During the polymerisations, olefin and diene can compete (Scheme 9), even if the diene is a better ligand, because in the π-allyl form of a resting species, only one site is vacant, and the terminal olefin, less bulky, is inserted in a ratio of 6–10%. After each olefin insertion leading to an alkyl species, two coordination sites are vacant and the coordination-insertion of the diene, which brings four electrons, occurs preferentially. So, it is possible to explain the mechanism of this highly uncommon copolymerisation, involving the insertion of only one olefin molecule between polyisoprene blocks.

5.2. Structure of the catalysts A–C

It should be possible now to propose formulas compatible with the common active species and with the observed differences of behaviour for the catalysts **A**, **B** and **C**. If we do not consider the ageing problems and the consecutive loss of activity observed for **C**, the **A**–**C** catalysts exhibited similar behaviour in the polymerisation experiments. However, the reaction times depend on the nature of the catalysts: **A** and **B** dissolved readily within 10–15 min, whereas the dissolution of **C** required few hours. With **B**, the polymerisations were slower: the obtention of a highly viscous medium required 4–5 h more than with **A**.



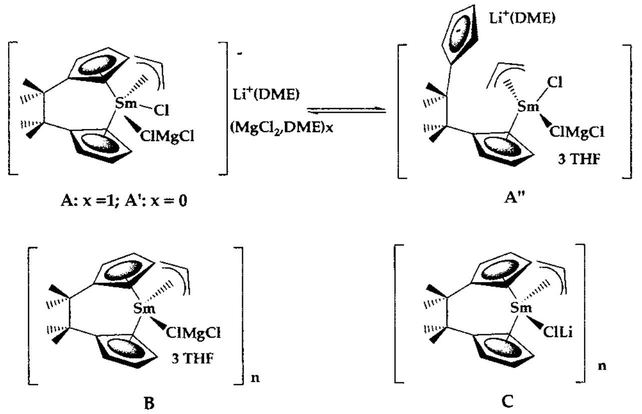
Scheme 9. The olefin/diene competition on the active allyl species.

5.2.1. Complex C

According to the NMR data, a polymeric formula $[(CMe_2C_5H_4)_2Sm(allyl)]_n$ could be proposed for **C**. Its insolubility in benzene and diene were therefore unexpected: an analogous complex, $[(CMe_3C_5H_4)_2Sm(allyl)]_n$, of red colour, was found well soluble in benzene, but inactive in the diene polymerisation whereas the nucleophilic carbene adduct $[C(N^iPr)_2(CMe)_2](CMe_3C_5H_4)_2Sm(allyl)$, a monomeric compound, showed some activity [10]. It had been assumed that $[(CMe_3C_5H_4)_2Sm(allyl)]_n$ remained highly associated in solution, and that isoprene did not possess the ability to enter in the coordination sphere and dissociate the starting material to give monomeric active species. Compared to this behaviour, the insolubility and the catalytic activity of **C** could be thought surprising and the proposed formula unsuitable. Moreover, because the ansa ligand is less sterically demanding than two $CMe_3C_5H_4$ ligands, the analogous complexes obtained with the chelating ligand $(CMe_2C_5H_4)_2$ usually present a higher coordination number. If $[(CMe_3C_5H_4)_2Sm(allyl)]_n$ is a stable molecule, the stable form for the analogous ansa complex would be $[(CMe_2C_5H_4)_2SmL(allyl)]_n$. The L ligand, not observed in the NMR spectra could be inorganic: the C, H elemental analysis of **C** (see Section 7) and the presence of Cl in the molecule (qualitative analysis) were satisfactory for the formula $[(CMe_2C_5H_4)_2Sm(allyl)LiCl]_n$. The formation of this bimetallic complex accounts for the difference in colour, yellow instead of red, and for the insolubility of **C** in aromatic solvents. In the ansa complex, with the presence of the ancillary ligand, the samarium atom is more electron rich, therefore the intermetallic associations are less strong and monomeric species can be formed, in the presence of diene which can, when used in large excess, displace the lithium chloride.

5.2.2. Complex B

The slowing down in the polymerisation reactions observed with **B** was initially related to the presence of THF, detected by NMR. As observed in NMR experiments, a five to tenfold excess of isoprene cannot displace the oxygenated ligand. This displacement slowly occurs when the diene is used in a very larger excess or when it is the solvent. During preliminary



Scheme 10. The catalysts **A**–**C**.

experiments [10], it had been established that the activity was clearly related to the presence of additional oxygenated ligands. Addition of one or two equivalents of THF decreased the reaction rate, and four equivalents impeded the activity.

Nevertheless, other reasons can also be considered: **B** contains magnesium, and the observed THF molecules would be in fact present in a $MgCl_2$ ligand as in the starting material, **2**. The formula, $[(CMe_2C_5H_4)_2Sm(allyl)MgCl_2(THF)_3]_n$ is proposed for the complex **B** which, contrary to **C**, was not obtained desolvated. It is the analogue of **C**, with $MgCl_2$ instead of LiCl. Catalytic systems including $MgCl_2$ were described: a mixture of a cerium complex, $(allyl)_3CeCl_5Mg_2(tmed)_2$ and alkylaluminium [22] catalyse isoprene polymerisation with a 50% *cis*-1,4 microstructure, the formation and the nature of the active species was not discussed. Titanium or zirconium Ziegler–Natta catalysts supported on $MgCl_2$ polymerise ethylene, propylene [23] or hexa-1,5-diene [24]. The tacticity can be increased, but with a decrease of the activity attributed to electrostatic interactions between the magnesium salt and the zirconium atom.

The rate decrease observed when **B** is used could be due to the same interaction.

5.2.3. Complex A

Complexes **A** and **A′** contain the $(CMe_2C_5H_4)_2$-Sm(allyl) moiety and as **B** also contain magnesium. **A** or **A′** dissolve readily in the neat diene, with the deposition of a very small quantity of an insoluble colourless powder during the polymerisations, which denotes the precipitation of salts. This precipitation is observed when **A** is used in catalytic amounts, in the pure diene or in a toluene–diene mixture, whereas this salts' elimination did not occur in concentrated toluene solution during the bulk synthesis. These facts indicate the presence of $MgCl_2$ as a ligand, displaced in the presence of diene. **A** and **A′** also contain lithium and the solids are pyrophoric, as if they contained a RLi reagent. The syntheses required two equivalents of allyllithium, and the formation of an anionic bisallylic complex, eventually dissociated in the presence of ligands or in coordinating solvents, could occur. Nevertheless the presence of only one paramagnetic allyl group was established by NMR. The search for a second allyl group in the diamagnetic range, in case of complete dissociation of the complex, failed. Moreover the RLi reagents polymerise the dienes with the formation of a high percentage of 1,4-*cis* polymer whereas **A** led quite exclusively to the 1,4-*trans*-polymer. As a summary, catalyst **A** is insoluble in aromatic solvents and contains lithium, the solid behaves as a RLi reagent when exposed to air but the presence of an allyllithium in diene or THF solution was not established. How would it be possible to propose an adequate formula for **A**, accounting for apparently incompatible properties?

It must be remembered that **A** (and **A′**) are obtained after treatment of the crude material with DME which is known to be a good complexant for the lithium cation, and therefore useful for the chloride ion activation [25]. The chloride ion could coordinate onto the samarium atom, allowing the formation of a non-associated, anionic, trimetallic compound of formula: $[(DME)Li][CMe_2C_5H_4]_2SmCl(allyl)MgCl_2(DME)]$. The **A** sample which contains two Mg per Sm atom would be a mixture of **A′** and of inorganic magnesium salt. The proposed structures for the three catalysts are represented in Scheme 10.

5.2.4. The ageing of the catalysts

There remain to understand which are the factors allowing the remarkable stability of **A**, stable for years while the other compounds bearing the $(CMe_2C_5H_4)_2$ ligand, and especially the chloride precursor, **1** and the catalyst **C** cannot be stored, or (for the alkyls) must be made and used in situ. It is possible to propose an explanation involving the strained nature of the bridge. A stable bridge between two Cp groups is offered by one carbon (or silicon) bridge [3a,26] or by a longer chain, three (or more) carbon atoms [27], allowing the required flexibility. The strain due to the $(CMe_2)_2$ group induces the intermolecular rearrangements encountered in the syntheses of the chlorides and alkyls (vide supra) and in the presence of additional metallic ions, might also cause intramolecular rearrangement. In DME solution, the ionic complex **A** can be dissociated in solvent-separated ion pairs. The lithium cation can migrate onto a Cp group, leading to a heterotrimetallic molecule, $(DME)Li(C_5H_4)(CMe_2)_2(C_5H_4)SmCl(allyl)MgCl_2(DME)$ without any chelating ligand on the samarium, **A″** (Scheme 10). Such a formula including a $Li(C_5H_4)$ fragment could explain the pyrophoric reaction of **A**. In the solid state, no rearrangements would take place in this non-strained, stable, molecule. In the polymerisation reactions, the non-polar medium favours the elimination of the salts and allows the return to a chelating form, $(CMe_2C_5H_4)_2[Sm]$.

6. Concluding remarks

The above presented results are illustrative of the difficulties encountered in the understanding of a catalytic system. It can be judged disappointing that the most satisfactory catalyst, easy to synthesise, stable for years would be a complex trimetallic association, the exact nature of which not being established, but only proposed. However, it was not a real problem to obtain reproducible polymerisation and copolymerisation experiments, new original and interesting materials were obtained and the organometallic concepts allowed to explain the mechanism of the copolymerisations.

The alkylation of the bimetallic Sm/Mg chloride, **2**, occurs on the magnesium atom, whereas the allylation occurs on the samarium. In fact, the substitution by the allyl group can occur in a first step on the more accessible magnesium atom, but the allyl group is then readily transferred onto the samarium. This difference of behaviour may be related to the better electron donating ability of the allyl reagent which brings four electrons, more efficient to displace the poorly reactive, bridged chloride ligand. The course of the allylation and alkylation reactions, conducted with **1** are different: the bisbutyl derivative $[(CMe_2C_5H_4)_2Sm(^{n}Bu)_2]Li$ is easily obtained while the formation of the bisallylic anionic complex $[(CMe_2C_5H_4)_2Sm(allyl)_2]Li$ does not occur, the complex $[(CMe_2C_5H_4)_2Sm(allyl)LiCl]_n$ is formed. The chemistry of the lanthanides, hard elements, is mainly governed by steric requirements, especially in the early series, and the role of the electronic factors in the reactivity of the lanthanide complexes remains largely in debate [28]. Nevertheless invoking steric reasons for the impossibility to form the bisallyl complex is not convincing because the $(CMe_2C_5H_4)_2$ moiety is not a bulky ligand. There is nowadays no decisive argument to explain the preference, in some cases, for a chloride towards an organic ligand. Because the organolanthanides are becoming highly implicated in the field of homogeneous catalysis, more efforts ought to be made in the near future to understand the rules of their formation and their stability in solution.

7. Experimental

7.1. Reagents and standards

All operations were performed under Ar using standard vacuum line techniques or in a Jacomex glovebox (O_2 < 2 ppm). Solvents were stored over sodium/benzophenone ketyl and vacuum transferred to the reaction vessels. MeLi (ether solution), Buli (*n*-hexane solution) were purchased from Aldrich. $SmCl_3(THF)_3$ [29], $Sm(BH_4)_3(THF)_3$ [30], $(C_5H_4CMe_2)_2SmCl(MgCl_2)(THF)]_4$ [14], allylLi(dioxane) [31], $LiCH_2TMS$ [32], $LiCH(TMS)_2$ [33] were obtained following published methods.

7.2. Measurements

^1H-NMR spectra were recorded in Bruker AC 200 or AC 300 spectrometers.

Elemental analyses were performed with a Fisons EA 1108 CHON apparatus.

SEC analyses were carried out in THF solutions (10 mg ml^{-1}, 20 °C, flow rate 1 ml min^{-1}) on a Gynkotek P 580A apparatus equipped with two Jordi Gel DVB mixed B columns and a IOTA2 refractive index detector. PS standards were used for column calibration and Mark–Houwink corrections were performed for determination of absolute values of molecular weights.

XPS experiments were performed using a Riber MAC2 instrument equipped with an Al anode (1486.6 eV) which operated at an acceleration voltage of 12 kV with an emission current of 25 ma (300 W). Emerging photoelectrons were analysed with detection normal to the surface. Windows were recorded around the $Sm3d_{5/2}$ (1083 eV) and the Sm4d (131 eV) peaks for Sm, around the Mg1s (1305 eV), Mg2s (90 eV), Mg2p (52 eV) peaks for the Mg and around Li1s (55 eV) for the Li, the peaks position are given in binding energy. The spectra were recorded with multiscan mode. The total resolution was ca. 1.2 eV. After smoothing, the background of all these peaks were removed by a Shirley routine and their area calculated. The Li1s area was calculated after desummation which was done by fitting with Gaussian (80%)–Lorentzian (20%) peaks, in the reason of the proximity of the Mg2p peaks. The peak areas were corrected by the sensitivity factors obtained from Scofield coefficients [17] multiplied by $1/\sqrt{E_{kin}}$.

7.3. Syntheses

7.3.1. $(Me_2CC_5H_4K)_2$

A THF solution of $(Me_2CCpH)_2$, (1.6 g, 7.47 mmol) was slowly added at −5 °C to a suspension (0.64 g, 16 mmol) of KH in THF. After the diene addition, the medium was allowed to rise at the room temperature (r.t.). The colour of the suspension turned from pale yellow to brown. After one night stirring, the suspension was filtered and the solvent removed. The solid was washed with toluene, and dried under vacuo to yield 1.93 g (89% yield) of a beige solid. Anal. Found: C, 64.59; H, 6.76. Calc. for $C_{16}H_{20}K_2$: C, 66.10; H, 6.94%.

7.3.2. *[(CMe$_2$C$_5$H$_4$)$_2$SmCl(THF)]$_2$ (**1**)*

(a) At r.t., a solution of (Me$_2$CC$_5$H$_4$K)$_2$ (290 mg, 1 mmol) in 20 ml of THF was slowly added to a THF solution of SmCl$_3$(THF)$_3$ (543 mg, 1.15 mmol). After 48 h stirring, a yellow solution and a brownish precipitate were formed. The solution was filtered, evaporated, leaving a paste which was extracted with toluene (40 ml). The slow evaporation of this toluene solution led to 200 mg of a yellow–beige solid (48% yield). Analytically pure yellow crystals, suitable for X-ray analysis, were obtained after slow crystallisation in a cold THF–pentane mixture. Anal. Found: C, 51.38; H, 5.44. Calc. for $C_{20}H_{28}OClSm$: C, 51.17; H, 5.97%.

X-ray analysis : the unit shell was identical to that previously described [13c].

(b) (Me$_2$CC$_5$H$_4$K)$_2$ (252 mg, 0.87 mmol) and SmCl$_3$(THF)$_3$ (411 mg, 0.87 mmol) were stirred in 40 ml of toluene during 24 h at 80–90 °C. A yellow–brown solution and a brownish precipitate were formed. The solution was filtered, the remaining salts washed with 10 ml of toluene, the combined toluene phases were concentrated to 5 ml. A beige powder was obtained, washed with cold toluene, and dried (230 mg, 56% yield). A sample was taken for NMR analysis in C$_6$D$_6$, the spectrum could not be interpreted. After pressurisation of the tube with THF vapour and stirring, the recorded spectrum was identical to that obtained for **1**.

7.3.3. *[(CMe$_2$C$_5$H$_4$)$_2$]$_3$Sm$_2$(THF)$_3$*

In an NMR tube, (Me$_2$CC$_5$H$_4$K)$_2$ (9.3 mg, 32 μmol) and SmCl$_3$(THF)$_3$ (10 mg, 21.3 μmol) and 0.5 ml C$_6$D$_6$ were heated for 1 h at 80 °C. The NMR spectrum of the orange solution showed only one set of signals: $\delta = 15.55$ (4H, Cp), 14.97 (8H, Cp), 13.88 (4H, Cp), 8.78 (8H, Cp), 2.36 (24H, Me) -4.16 (12H, Me) 2.75 (24H, THF) -1.0 (24H, THF). After removal of the solvent, drying under vacuum and redissolution in C$_6$D$_6$, only 3 THF were present, signals at $\delta = 15.91$ (8H), 15.80 (4H), 10.80 (4H), 8.89 (8H), 2.38 (24H), -4.32 (12H), 2.17 (12H), -0.60 (12H).

7.3.4. *[(CMe$_2$C$_5$H$_4$)$_2$SmBH$_4$(THF)]$_2$*

THF (20 ml) was condensed on a mixture of 1 g (3.44 mmol) of (Me$_2$CC$_5$H$_4$K)$_2$ and 1.42 g (3.45 mmol) of Sm(BH$_4$)$_3$(THF)$_3$. The mixture turned yellow and was stirred for 4 h at r.t., then filtered. The precipitate was washed with cold pentane. A yellow solid (1.25 g, 76%) was obtained. ^{1}H-NMR: $\delta = 14.69$ (4H, Cp), 7.95 (4H, Cp), 1.79 (6H, Me), -0.38 (4H, THF), -0.70 (4H, THF), -18.0 (4H, BH$_4$). IR (nujol film) $\nu = 2431$, 2274, 2211 cm^{-1}.

The compound was dissolved and crystallised in toluene, the yellow crystals, after a long drying under vacuum became insoluble in toluene.

7.3.5. *Catalyst **A** [(CMe$_2$C$_5$H$_4$)$_2$SmCl(allyl)MgCl$_2$-(DME)]Li(DME), MgCl$_2$*

(CMe$_2$C$_5$H$_4$MgCl)$_2$(THF)$_4$(650 mg, 1.05 mmol) and SmCl$_3$(THF)$_3$ (500 mg, 1.05 mmol) were weighed in a 50 ml vessel, 25 ml toluene was condensed and the mixture was stirred for 2 h at r.t. The yellow–orange solution was filtered and a yellow–brown precipitate was discarded. The solution was poured at -30 °C under vigorous stirring on 315 mg of allyllithium–dioxane (0.23 mmol). Upon rising at r.t., the deep red solution was filtered and the solvent was removed under vacuum. The expanded oil was dissolved in 15 ml DME and the solvent pumped off. After washing the expanded solid with Et$_2$O, 485 mg of a red–brown powder was isolated (78% yield). XPS analysis: Sm/Mg/Li = 1:2:1. NMR data, see Table 2.

7.3.6. *Catalyst **A**′*

The expanded oil obtained as above was dissolved in a small volume of DME and the addition of Et$_2$O led to a microcrystalline brick-red powder in 30% yield. XPS analysis Sm/Mg/Li = 1:1:1.

7.3.7. *Catalyst **B***
[(CMe$_2$C$_5$H$_4$)$_2$Sm(allyl)MgCl$_2$(THF)$_3$]$_n$

(CMe$_2$C$_5$H$_4$MgCl)$_2$(THF)$_4$ (420 mg (0.68 mmol)) and 323 mg (0.68 mmol) of SmCl$_3$(THF)$_3$ were mixed in 20 ml toluene, and magnetically stirred at r.t. during 2 h, leaving a yellow–orange solution and a small amount of a beige precipitate, eliminated by filtration. After addition of the toluenic solution on 210 mg (1.55 mmol) of allylLi(diox), the colour became burgundy red. The mixture was magnetically stirred for 30 min, the greyish precipitate eliminated and the solvent evaporated. Dioxane was added, the solution was concentrated and ether added, no crystallisation occurred. The solvents were removed, THF was added and the solution was evaporated again and toluene condensed, allowing the precipitation of salts, eliminated by filtration. After evaporation to dryness, a red–brown solid (369 mg, 76% yield) was obtained after condensation of 20 ml ether on the red expanded oil and removal of the ether. XPS analysis Sm/Mg/Li = 1:1:0. NMR data, see Table 2.

7.3.8. *Catalyst **C**: [(CMe$_2$C$_5$H$_4$)$_2$Sm(allyl)LiCl]$_n$*

(Me$_2$CC$_5$H$_4$K)$_2$ (154 mg (0.53 mmol) and 250 mg (0.53 mmol) of SmCl$_3$(THF)$_3$ were mixed in 30 ml of toluene, stirred by sonication during 30 min and magnetically stirred at 60–65 °C for 30 h, leaving a yellow solution and a yellow–beige precipitate. After addition of 72 mg (0.53 mmol) of allylLi(diox), the colour became intense red within 5 min. The mixture was stirred 5 min by ultra sounds, magnetically stirred half an hour, filtrated to eliminate the lithium and potassium salts and slowly evaporated. The crude material, a mixture of yellow and orange–red powders turned to a deep red oil by exposure to THF vapour. Extraction with ether allowed the formation of a yellow precipitate (150 mg). After evaporation of the ether, dioxane was added, forming a red solution and evaporated giving a second crop of yellow material (180 mg). Total yield 70%. Anal. Found: C, 51.68; H, 5.88. Calc. for $C_{19}H_{25}ClLiSm$: C, 51.17; H, 5.61%. NMR data, see Table 2.

7.3.9. Alkylations

In the glove box, the stoichiometric amount of alkylating reagents was introduced in a C_6D_6 solution of ca. 10 mg of chloride **1** or **2**. After 1 h stirring, the solvent was removed, the residue pumped off and 0.5 ml C_6D_6 were added to dissolve the orange viscous oil. The NMR spectra show the formation of the alkyl compounds (Table 4).

7.3.10. Isoprene polymerisation

In the glove box, 10 mg of catalyst **A** and 1 ml of isoprene were poured in a 20 ml vessel equipped with a magnetic stirrer. The vessel was connected to the vacuum line and the mixture vigorously stirred for 24 h at 50 °C. The flask was opened to air and an adequate amount of solvent was added until complete dissolution. The polymer was precipitated by pouring the solution in 100 ml EtOH. The solid was isolated and dried under reduced pressure for 24 h; 100% yield (95% *trans*-polyisoprene containing small amounts ca. 3% of 3,4- and ca. 2% of 1,4-*cis*-polyisoprene) $M_n = 50\,000$, PDI = 1.32.

7.3.11. Isoprene/hex-1-ene copolymerisation

Catalyst **A** (10 mg) was weighed in a 20 ml flask, 1 ml of isoprene and 1 ml of hex-1-ene are poured in the flask with a syringe (ratio isoprene/catalyst = ca. 500). The flask was placed in a thermostatic bath at 50 °C and the mixture was magnetically stirred for 24 h. The flask was open, then 5 ml of toluene was added to the viscous mixture to dissolve the polymer and the solution was poured into 100 ml of EtOH. The polymer was washed twice with EtOH and dried 24 h under vacuum; 95% yield, $M_n = 33000$, PDI = 1.58; inserted hex-1-ene: 11.4%. The same experiments performed with catalysts **B** and **C** give very similar results.

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