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# Organolanthanides, catalysts for specific olefin-diene copolymerization: access to new materials

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## Abstract

Non-hindered ansa dicyclopentadienylallyl complexes of samarium, $[(CMe_2C_5H_4)_2Sm(allyl)]_n$, and $(CMe_2C_5H_4)_2Sm(allyl)L$ (L=THF or allylLi) polymerize isoprene without an aluminum cocatalyst. The polymerizations are highly stereospecific, affording nearly quantitatively 1–4 *trans* polyisoprene. In the presence of linear 1-olefins, copolymers are formed, with 6–10% of olefin inserted; the 1–4 *trans* structure of the polyisoprene chain is not altered, and only one olefin molecule is inserted between two polyisoprene fragments. In the common initiator of these three catalytic systems, the $(CMe_2C_5H_4)_2Sm(allyl)$ moiety, only one vacant site would be available. As a consequence of the presence of the alkyl aliphatic chain, the viscoelastic behaviour of the branched copolymers markedly differs from that of *trans* 1–4 polyisoprene: an important loss of crystallinity and a dramatic decrease of the Young modulus are observed; the copolymers show elastomeric properties.

*Keywords:* Allylic complexes; Catalysis; Polymerization; Lanthanide; Samarium

## 1. Introduction

Copolymers of dienes with 1-alkenes could be materials of commercial importance, for example as alternative to natural rubber [1–4]. To obtain them remains an actual challenge, because usually dienes, better ligands, are poisons for olefin polymerization [5]. By using strained ansa dicyclopentadienylneodymium or samarium allyl complexes as catalyst, and without an aluminum co-catalyst, it was possible to copolymerize isoprene and 1-hexene [6] or longer ($C_8$–$C_{18}$) 1-olefins [7]. About 10% of olefin was incorporated in the polymer, one molecule of olefin being inserted between blocks of *trans* 1–4 polyisoprene. It is noteworthy that the physical properties of the branched polymers markedly differ from those of *trans* 1–4 polyisoprene.

It was of importance to study this original catalytic system to understand why and how the particular organometallic structure allowed the copolymerization.

## 2. Experimental

All work was carried out under argon with carefully dried and degassed solvents and monomers (isoprene and terminal olefins). The catalysts have been prepared using standard procedures involving glove box and vacuum line techniques. They were kept in a glove box under an argon atmosphere. Determination of the metal contents were made by XPS after calcination of the samples. The polymerization experiments were conducted in a glass flask, in a thermostatic bath at 50°C, for a given time when a solvent, hexane or toluene, was used, or until the mixture became highly viscous. The total volume of the liquid phase was 1–5 ml, the molar ratio catalyst/monomer or comonomers was $10^{-3}/1$. The polymerizations were stopped by opening to the air. After dissolution in hot toluene, the copolymer products were precipitated with ethanol and dried under reduced pressure. The polymers were analyzed by $^1H$ and $^{13}C$ NMR. The molecular weights were determined by GPC or viscosimetry.

The identification of the chain ends was made on a sample of low molecular weight, obtained by stopping the

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reaction after 1 h and elimination of the remaining monomers under reduced pressure.

## 3. Results and discussion

### 3.1. Catalysts preparation

A convenient precursor incorporating the ansabiscyclopentadienyl ligand $[CMe_2(C_5H_4)]_2$ was described: $[(CMe_2C_5H_4)_2SmCl(THF)]_2$ (**1**). Two different syntheses were published, the first one used the samarium metal to promote the fulvene coupling, a subsequent oxidation with tert-butylchloride leading to the chloride **1** [8]. The other [9] used a magnesium reagent [10], $(CMe_2C_5H_4MgCl)_2(THF)_4$ (Scheme 1).

We did not obtain any crude product of satisfactory purity (NMR control) following method 1. Following method 2, a reaction was first conducted at the NMR scale, the $^1H$ NMR spectrum showed the presence of four THF per samarium atom. The intensity of these signals did not decrease after two cycles of toluene addition and evaporation. Unexpectedly, the addition of $LiCH_2SiMe_3$ or $LiCH(SiMe_3)_2$ did not allow to obtain paramagnetic [Sm]-R species. We considered with more attention the described experimental parts and it appeared that the almost identical work-up allowed the formation of two different compounds, crystals of the chloride **1** and of another derivative, **2**, including a magnesium salt in the molecule, $[(CMe_2C_5H_4)_2SmCl(MgCl_2{\cdot}3THF),THF]_2$ [11]. Their X-ray crystal structures were established but nothing allowed to determine the nature of the bulk materials, in particular the NMR data of the soluble paramagnetic complex **2** were not available. We estimated, on the basis of the NMR studies, that the crude material was essentially the mixed samarium–magnesium compound. A bulk synthesis was performed, and a crude material was obtained as an yellow–orange powder. Attempts to eliminate the magnesium chloride, by extraction with non-polar solvents and by crystallisation failed, in all cases the only noticeable result was the recovering of a material with an altered NMR spectrum (broadening of the CpH signals and presence of numerous new signals).

To avoid the presence of the magnesium salt, we used the potassium salt of the chelating dianion obtained by the reaction of KH on the corresponding diene [10]. In this case, the NMR spectrum of the crude material showed the normal integration value of the THF signals. After crystallisation, analytically pure **1** was obtained. This pure complex was only moderately soluble in deuterated benzene.

By addition of allyllithium (dioxane adduct) to the organolanthanides **1** and **2**, three catalysts were prepared:

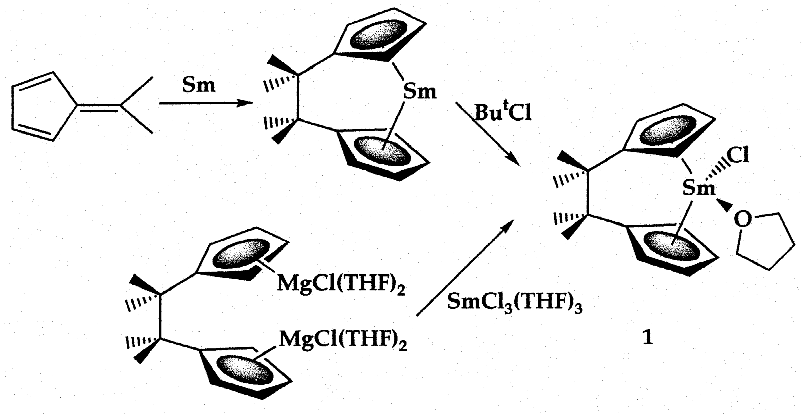
(**A**): addition of one molar equivalent of allyllithium to a THF solution of **1**. After toluene extraction, removal of the solvent yielded **A**, as a yellow powder. **A** was not soluble in benzene but after addition of one molar equivalent of THF or amine, deep red soluble adducts were formed. The same colour had been observed in the $C_5H_4$ $^tBu$ series: the adducts $(^tBuC_5H_4)_2Sm(allyl)L$ are red [12].

(**B**) and (**C**): to be sure that not only the magnesium but also the samarium would be alkylated, two molar equivalents of allyllithium were added to a toluene solution of (**2**). After elimination of the salts, and evaporation to dryness:

- The crude material was dissolved in THF, and the solution slowly concentrated to a red oil. A tan solid, **B**, was finally obtained after trituration in pentane. **B** was sparingly soluble in $C_6D_6$.
- To displace the THF and dioxane residues, dimethoxyethane was added. A crystallisation in ether afforded a rosa–brown powder, **C**, insoluble in non-polar solvents.

### 3.2. Polymerizations

Using **A**, **B**, and **C** as catalysts, the isoprene polymerization was highly stereospecific, 1–4 *trans* polyiso-



Scheme 1.

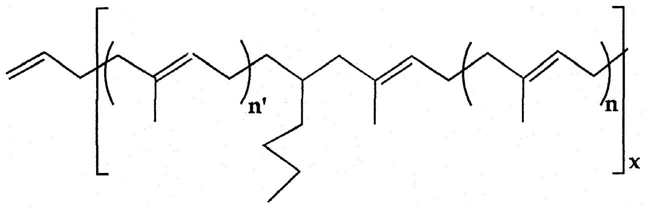


Fig. 1. The inserted olefin in the polymeric chain.

prene was nearly quantitatively obtained. These results are in good accordance with previous reports on the reactivity of LiLn(allyl)$_4$ [13] and of Ln(allyl)$_3$ [14] towards butadiene.

In the absence of solvent, the total conversion of the crude monomer required about 16–24 h. In non-polar solvents, the reactions run faster (5–8 h). Addition of THF impeded the polymerization. The reaction time were slightly different because **C** dissolved readily in the neat isoprene, whereas from **A** and **B**, a suspension could be observed during a half or a few hours.

Because **B** and **C** were obtained by using two molar equivalents of allyl lithium per samarium, a polymerization was conducted with the dioxane adduct ($C_3H_5$)Li($C_4H_8O_2$) as catalyst, in order to estimate the participation of an allyl moiety to the reaction. The results were quite different: a high contents of *cis* 1–4 polyisoprene was obtained. Considering the *trans* 1–4 microstructure of the polymers obtained with **B** and **C**, it is clear that an anionic allyl moiety is not directly involved in these polymerizations.

In the presence of terminal olefins (hexene, octene, decene, octadecene), with catalysts **A**, **B**, and **C,** copolymer were formed, containing ca. 10% of olefin. The 1–4 *trans* structure of the polyisoprene chain was not altered, and only one molecule of olefin was inserted between two polyisoprene fragments (Fig. 1). Only linear terminal olefins could be inserted. It is noteworthy that for the rare examples of butadiene insertion in polyethylene chains, the diene incorporation also occurred in a 1–4 *trans* fashion [5,15].

### 3.3. Polymer characterization

The microstructure of the polymers were determined by $^1$H and $^{13}$C NMR. The presence of the vinyl group as chain end was established by NMR studies of crude samples of low molecular weight. The ratio inserted 1-olefin/isoprene was estimated from the integral values of the $^1$H NMR terminal methyl signal of the inserted aliphatic chain at ca. 1.05 ppm and of the methine signal of polyisoprene at 5.4 ppm. Yields of copolymerization reactions were estimated taking notice of the ratio (6–10%) of inserted 1-olefin:

$$\text{Yield}\,\% = m_{\text{co-polymer}}/m_{\text{isoprene}} + m_{\text{inserted olefin}}$$

In Table 1 are summarized the experimental results and the most interesting characteristics of the copolymers and of *cis* and *trans* polyisoprenes.

The insertion of an alkyl chain modifies dramatically the thermal and mechanical properties of the copolymers. The decreasing of the $T_g$, introduces an internal plastification of the amorphous part, whereas the decreasing of $\Delta H$ and Young modulus show the important loss of crystallinity [16]. Thus, insertion of a small percentage of an olefin bearing an alkyl chain, in a crystalline transpolyisoprene, confers to the copolymers an elastomeric behaviour.

### 3.4. Nature of the precursors

Catalysts **B** and **C**, obtained from **2**, contained a large amount of magnesium salts, whose quantity varied with the samples, following the quality of the last crystallisation. The presence of magnesium may be illustrative of the well-known difficulty to separate the organolanthanide complexes from the inorganic salts during the syntheses. Thus, these catalysts are in fact organolanthanide mixed with an inorganic magnesium salt, but one cannot absolutely exclude that this salt would be a ligand as in the starting material **2**.

Taking the available analytical data (NMR, XPS, solubility) into account, the following formulas could be proposed: (**A**) [($CMe_2C_5H_4$)$_2$Sm(allyl)]$_n$; (**B**) and (**C**)

Table 1
Characteristics of polyisoprenes and copolymers

| | *Trans* PI | $C_6$ | $C_8$ | $C_{10}$ | $C_{18}$ | *Cis* PI |
|---|---|---|---|---|---|---|
| Yield (%) | 100 | 95 | 100 | 98 | 100 | |
| Inserted olefin (%) | | 11.4 | 6 | 6 | 6.8 | |
| $M_n \times 10^3$ | 41 | 33 | 43 | 40 | 64 | |
| $M_w \times 10^3$ | 52 | 52 | 66 | 74 | 91 | |
| $M_{WD}$ | 1.27 | 1.58 | 1.54 | 1.84 | 1.42 | |
| $T_g$ (°C) | −64.9 | −66.3 | −70.5 | −75 | −67.8 | −64 |
| $T_m$ (°C) | 46 | 38.3 | 36.2 | 36 | 19.2 | – |
| $\Delta H$ (J/g) | 60 | 3.5 | 3.9 | 1.6 | 33 | – |
| *E* (Mpa) | 70 | 12 | 2 | 2 | 8 | 2 |

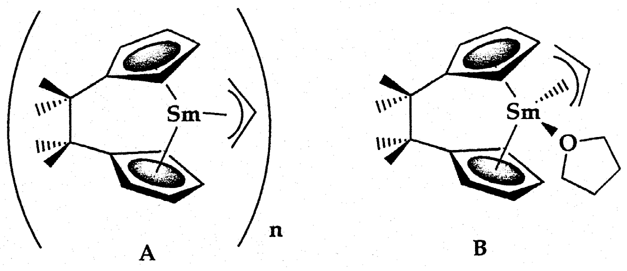


Fig. 2. A tris(ansabicyclopentadienyl) nuclear complex.

(free of magnesium salt), $(CMe_2C_5H_4)_2Sm(allyl)(THF)$ and $(CMe_2C_5H_4)_2Sm(allyl)_2(LiDME)$. These three catalysts would only differ by the ancillary ligands: none, THF or allylLi for **A**, **B** and **C**, respectively (Fig. 2).

Obtaining **B** does not require — a priori — the use of two equivalents of allyllithium. An attempted synthesis was made with one equivalent, the results were not convincing, as part of the starting material was recovered. The excess of reagent may be necessary for kinetic reasons.

For **C**, the insolubility and the presence of lithium and dimethoxyethane speaks in favor of the formation of an anionic complex, $(CMe_2C_5H_4)_2Sm(allyl)_2(LiDME)$, as frequently observed in lanthanide organometallic chemistry [17]. However, in the $^1H$ NMR spectrum, only one allyl ligand per samarium is observed. A dynamic equilibrium (Scheme 2) between the anionic and the neutral (THF solvated) form may be invoked, but the lithium counterion might be also a chloride anion, therefore the isolated solid **C** would be, in this case, $(CMe_2C_5H_4)_2SmCl(allyl)(LiDME)$.

### 3.5. Nature of the active species

The catalyst **A**, **B** and **C** allowed the formation of the same polymers, with similar low molecular weight distribution. This could indicate the formation of the same active species: these three catalysts have an identical organometallic core, $(CMe_2C_5H_4)_2Sm(allyl)$, and differ only by the ancillary ligands. During the polymerization experiments conducted with **A**, the color slowly turned to pale brown denoting therefore an increase of the coordination number in the presence of the monomer. The undissolved **B** could be observed in the polymerization medium during a few hours, indicating that the displacement of the ancillary ligand by the diene is rather slow. The dissolution of **C** in the neat isoprene began within minutes, indicating the concomitant, easy, formation of a neutral species.

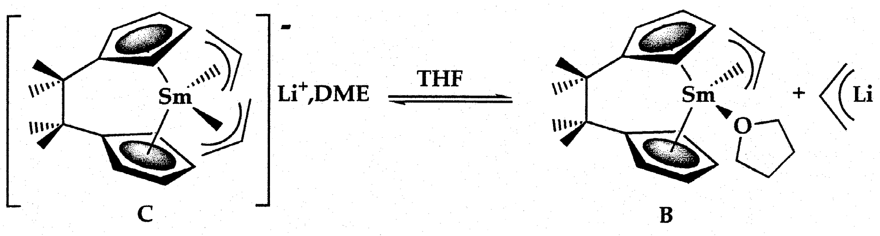
Isolated and well-characterized complexes including the $(CMe_2C_5H_4)_2$ ligand are dimeric samarium chlorides, in which the central atom is pentacoordinated [8,11]. The corresponding allylic moiety $(CMe_2C_5H_4)_2Sm(allyl)$ could offer two vacant sites, or only one, assuming that the allyl anion supplies two electrons more than a chloride anion. Considering that the olefin is able to compete with the diene ligand, we postulate that only one vacant site is available, allowing a 1–2 coordination of the diene, leading to a *trans* 1–4 polyisoprene.

### 3.6. Ageing of the catalysts

Samples of **A** and **C** were stored at ambient temperature in a glove box. After 3 months, **A** became inactive, its NMR spectrum was found deeply altered: obviously the initial structure of **A** was lost. On the contrary, the catalytic activity of a sample of **C** prepared 2 years ago has not markedly altered. The NMR spectrum denoted only some rearrangement: a set of known signals (ca. 15% by the integration of CpH signals) attributed to a tris-cyclopentadienyl compound (vide infra) was present. The compound **B** was only recently synthesized and therefore its stability is at the moment unknown.

The poor stability of the catalyst **A** is not a unique feature. Other related complexes were also unstable: a yellow microcrystalline powder of **1** which seemed non-altered after 6 months, was controlled by NMR: only traces of the starting material were observed. The complex **2** cannot be handled without a considerable alteration, the best way to use it is to make it in situ avoiding the isolation step; the same observations were made for alkyl complexes obtained from **1**. During the NMR-monitored syntheses of **1**, the transient formation of a tris-cyclopentadienyl complex (Fig. 3) was evidenced.

In some cases, the presence of this compound in the altered catalysts was established, but the characteristic features, solubility, complexity of the NMR spectra, reactivity, denoted above all the formation of highly associated structures. The driving force for such disappointing evolu-



Scheme 2.

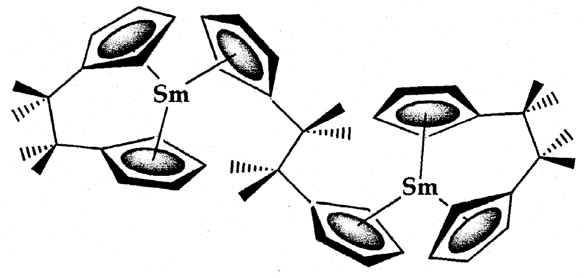


Fig. 3. Proposed structures for A and B complexes.

tion could be the strain of the structure: a stable bridge between two Cp groups has to be made of less or more than two atoms: $SiMe_2$ [18] or $(CH_2)_3$ [19], for example; the $CMe_2$–$CMe_2$ bridge may be a factor of destabilisation. After some time in the solid state, the strained chelating bridge could lead to more stable intermetallic bridges, and strong associations may be formed.

On the contrary, **C** was found fairly stable and could be stored for years. Its molecular arrangement, at least in the solid state, might be different: the chelating $(CMe_2C_5H_4)_2$ ligand may be associated to different metals: one samarium and one lithium atom. In this case no strain is imposed on the samarium moiety. In a non-polar medium the extrusion of a neutral molecule (allylLi or LiCl) would regenerate the bridged $(CMe_2C_5H_4)_2$ Sm moiety of the catalyst.

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