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C_5Me_5/ER-Ligated samarium(II) complexes (ER=OAr, SAr, NR^1R^2): a new type of olefin polymerization catalysts

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Abstract

The synthesis and polymerization reactions of a series of C_5Me_5/ER-ligated lanthanide(II) complexes (ER=OAr, SAr, NR^1R^2) are described. In sharp contrast with the previously known metallocene complexes, this type of heteroleptic samarium(II) complex acts as a unique catalytic system, which cannot only polymerize styrene and ethylene, but also copolymerize them into block styrene–ethylene copolymers in the presence of both monomers. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Chemical synthesis; Copolymerization; Crystal structure; Lanthanides; Pentamethylcyclopentadienyl; Thiolate

1. Introduction

There has been intense recent interest in the use of well-defined group 4 and group 3/lanthanide metal complexes as catalysts or precatalysts for polymerization of olefins [1–7]. Among these catalytic systems, the lanthanide (including group 3) metal-based catalysts have a potential advantage over group 4 metal analogs, since they do not require a co-catalyst to show high reactivity. However, most of the lanthanide catalysts reported so far have been based on complexes which bear two sterically demanding C_5Me_5 ligands [4–6]. These metallocene complexes are active for ethylene polymerization, but not able to polymerize substituted olefins [8–14].[1]

We present herein a new type of lanthanide(II) complex with mixed C_5Me_5/ER-ligands (ER=OAr, SAr, NR^1R^2), which was recently developed in our laboratories. This type of complex, particularly that of samarium(II), acts as a very unique catalytic system which not only polymerizes but also copolymerizes styrene and ethylene.

2. Synthesis of lanthanide(II) complexes with mixed C_5Me_5/ER ligands

Our approaches to a lanthanide(II) complex with mixed C_5Me_5/ER ligands started with the metathetical reaction of the samarium(II) bis(aryloxide) complex $(ArO)_2Sm(THF)_3$ (Ar=$C_6H_2^tBu_2$-2,6-Me-4) [15] with 1 equiv of KC_5Me_5 (Scheme 1) [16]. The final product obtained in this reaction was not the expected simple C_5Me_5/OAr-ligated samarium(II) complex **A**, but its KC_5Me_5 adduct **1a** (Scheme 1). Complex **1a** could also be obtained more efficiently by the reaction of $(C_5Me_5)_2Sm(THF)_2$ with 1 equiv of KOAr, as shown in Scheme 1 [16]. This reaction is quite general and can be extended to the synthesis of similar lanthanide(II) complexes (**1b–f**) bearing other anionic monodentate ligands, such as thiolates and amides (Scheme 2) (Z. Hou, Y. Wakatsuki, unpublished result) [17]. Complexes **1a–f** all can be viewed as a C_5Me_5/ER-ligated Ln(II) complex (Ln=Sm or Yb) coordinated by a neutral '$C_5Me_5K(THF)_n$' ligand [16]. These complexes all adopt a similar polymeric structure via 'intermolecular' interaction between the K atom and a C_5Me_5 ligand. X-ray structures of **1b** and **1c** are shown in Figs. 1 and 2, respectively (Z. Hou, Y. Wakatsuki, unpublished result).

The K-free, C_5Me_5/OAr-ligated Sm(II) complex **2**, which adopts a dimeric structure via μ-OAr bridges, could

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[1] Polymerization of α-olefins by group 3 or lanthanide metal complexes with modified cyclopentadienyl ligands has been recently reported. For examples, see Refs. [12–14].

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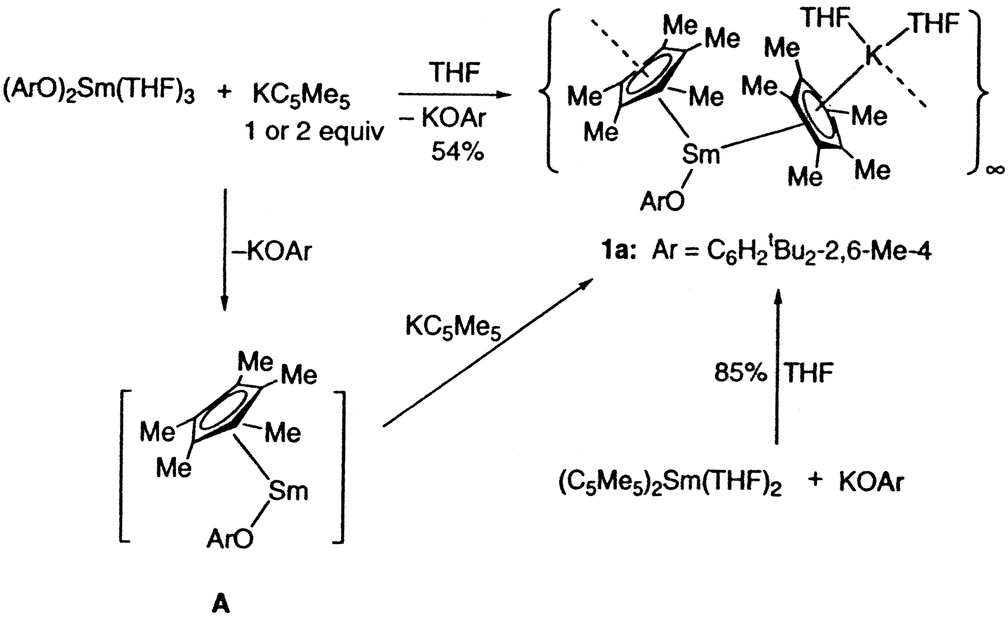


Scheme 1.

be synthesized in high yields by the reaction of $(C_5Me_5)_2Sm(THF)_2$ with 1 equiv of ArOH or $(ArO)_2Sm(THF)_3$ in toluene, as shown in Scheme 3 [16]. Reaction of **2** with 2 equiv of KC_5Me_5 yields **1a**, while treatment of **2** with 4 equiv of hexamethylphosphoric triamide (HMPA) affords the monomeric complex **3** in high yields (Scheme 3) [16].

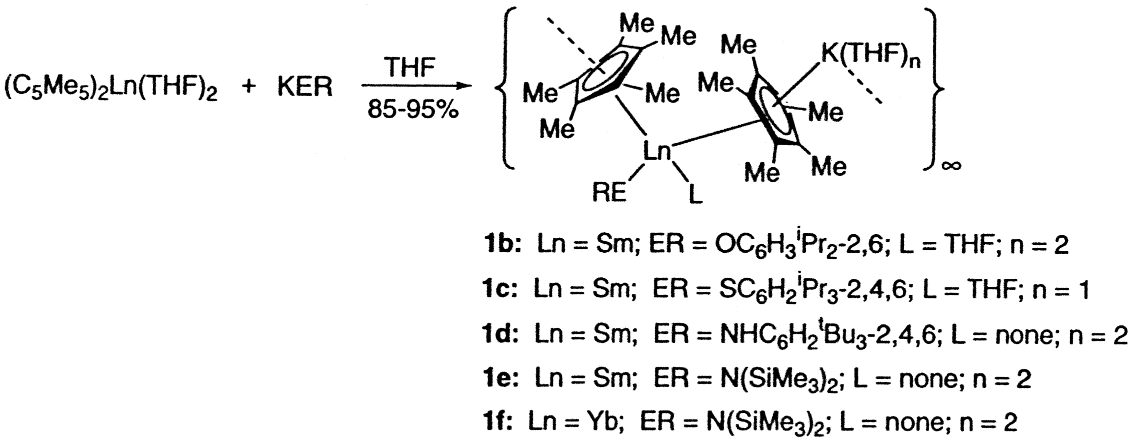
The reaction of the polymeric **1a** or **1e** with 2 equiv of HMPA (per Sm) yielded almost quantitatively the K-free, monomeric complexes **3** or **4**, respectively (Scheme 4) (Z. Hou, Y. Wakatsuki, unpublished result) [16], which again demonstrates that the '$C_5Me_5K(THF)_n$' unit in **1a–f** can be viewed as a neutral ligand. These results also suggested that generation of a sterically unsaturated, highly reactive Ln(II) species, such as '$(C_5Me_5)Ln(ER)$', could be possible, if the neutral '$C_5Me_5K(THF)_n$' ligand in **1a–f** is dissociated from the lanthanide atom.

Based on this assumption, the reactivity of this new type of lanthanide(II) complex towards some olefin monomers was examined.

3. Polymerization of styrene

The results of the polymerization of styrene by several types of lanthanide(II) complexes are summarized in Table 1.

The reaction of the unsolvated samarium(II) complex $(C_5Me_5)_2Sm$ with an excess of styrene has been reported to yield a stable bimetallic complex, $(C_5Me_5)_2Sm(\mu$-



Scheme 2.

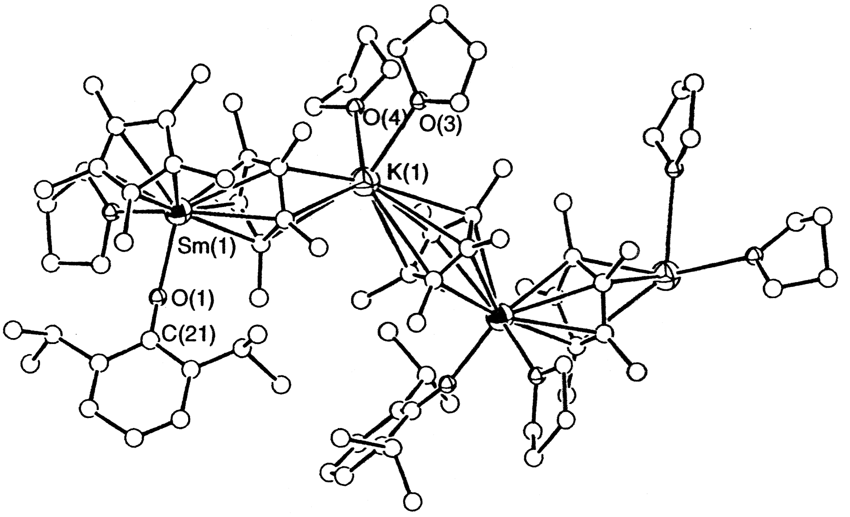


Fig. 1. X-ray structure of **1b**. ∠Sm(1)–O(1)–C(21): 165(1)°.

$CH_2CHPh)Sm(C_5Me_5)_2$ [11], which is inert toward polymerization of styrene [11,18]. The solvated homoleptic samarium(II) complexes $(C_5Me_5)_2Sm(THF)_2$, $Sm(OAr)_2(THF)_3$, or $Sm(N(SiMe_3)_2)_2(THF)_2$ did not react with styrene at room temperature (runs 1–3, Table 1). Neither did the dimeric complex **2** or the HMPA-coordinated complex **3** (runs 10–11, Table 1).

In contrast, the C_5Me_5/ER-ligated Sm(II) complexes **1a–e**, which contain the neutral '$C_5Me_5K(THF)_n$' ligand, all showed a high activity for the polymerization of styrene. In addition, ER-ligand dependence of the activity was also observed. Complex **1b**, which bears a less bulky $OC_6H_3{}^iPr_2$-2,6 ligand, is more active than the 4-Me-2,6-$^tBu_2C_6H_2O$-ligated complex **1a** (runs 4 and 5, Table 1). The more electron-donating amide complexes **1d,e** showed a higher activity than the aryloxide and thiolate complexes

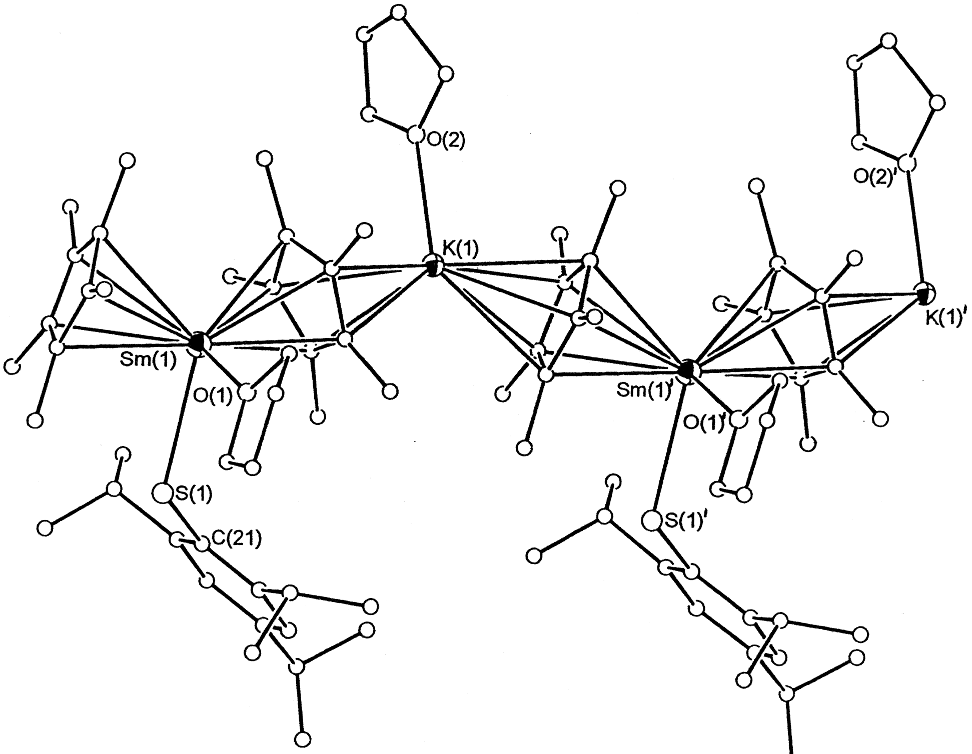
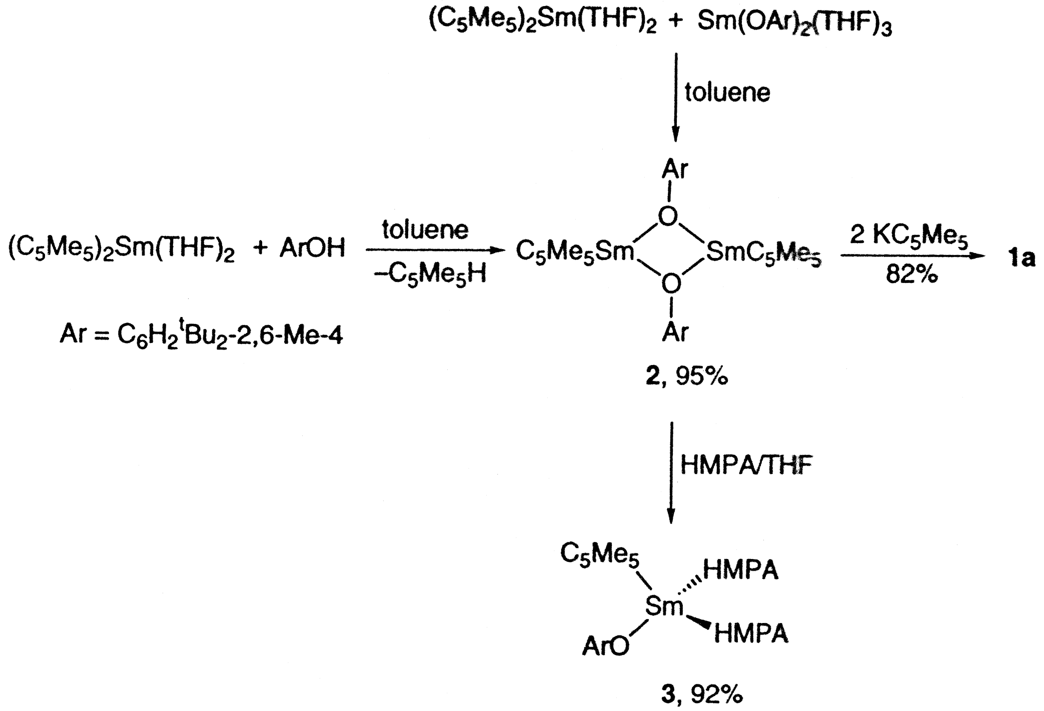
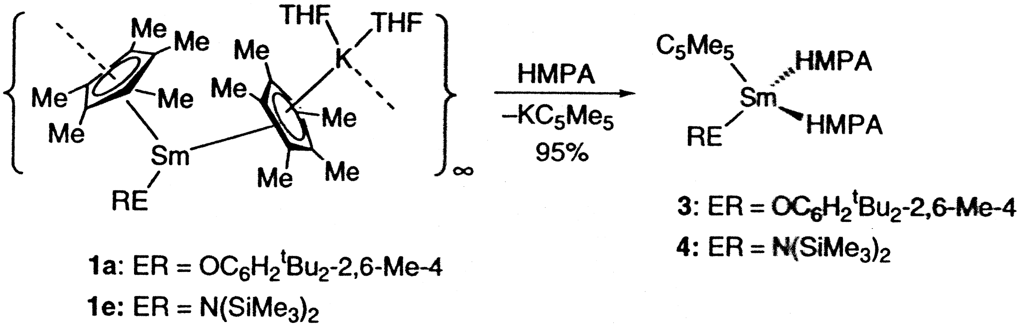


Fig. 2. X-ray structure of **1c**. ∠Sm(1)–S(1)–C(21): 124.0(8)°.



Scheme 3.



Scheme 4.

Table 1
Polymerization of styrene by lanthanide(II) complexes[a]

Run	Cat	Run time	Yield (%)	M_n ($\times 10^{-4}$)[b]	M_w/M_n[b]
1	$(C_5Me_5)_2Sm(THF)_{0\ or\ 2}$	1 day	0	–	–
2	$Sm(OAr)_2(THF)_3$	1 day	0	–	–
3	$Sm(N(SiMe_3)_2)_2(THF)_2$	1 day	0	–	–
4	**1a**	30 min	89	34.7	1.73
5	**1b**	30 min	100	24.5	1.93
6	**1c**	150 min	79	17.1	1.45
7	**1d**	20 min	100	14.4	2.16
8	**1e**	10 min	100	8.2	2.45
9	**1f**	1 day	0	–	–
10	**2**	1 day	0	–	–
11	**3**	1 day	0	–	–

[a] Conditions: Sm(II) compound, 0.05 mmol; styrene, 4 ml; toluene, 10 ml; room temperature.

[b] Determined at 135°C against polystyrene standard by GPC.

Table 2
Polymerization of ethylene by lanthanide(II) complexes bearing mixed C_5Me_5/ER ligands[a]

Run	Cat	Run time	Yield (g)	M_n ($\times10^{-4}$)[b]	M_w/M_n[b]
1	**1a**	20 min	3.00	45.0	2.75
2	**1b**	10 min	1.00	33.0	2.49
3	**1c**	10 min	0.99	58.0	1.79
4	**1d**	10 min	0.48	49.7	2.90
5	**1e**	30 min	0.55	309.9	2.83
6	**1f**	2 h	0	–	–

[a] Reaction conditions: a precatalyst, 0.05 mmol; ethylene, 1 atm; toluene, 15 ml; room temperature.

[b] Determined at 135°C against polystyrene standard by GPC.

1a and **1c** (runs 4, 6, 7 and 8, Table 1). The ytterbium(II) complex **1f** is not active for the polymerization of styrene, showing that the reducing power of the lanthanide(II) ions plays a critically important role in the present polymerization reaction.[2]

4. Polymerization of ethylene

The samarium(II) complexes **1a–e** also showed high activity for ethylene polymerization, giving linear polyethylene with M_n up to 3×10^6 (based on polystyrene standard) (Table 2). Among these catalysts, the 4-Me-2,6-$^tBu_2C_6H_2O$-ligated complex **1a** showed the highest activity (run 1, Table 2), while the $(Me_3Si)_2N$-ligated complex **1e** gave the highest molecular weight of polyethylene (run 5, Table 2). The ytterbium(II) complex **1f** was again inert for polymerization of ethylene (run 6, Table 2).

5. Block copolymerization of styrene and ethylene

The C_5Me_5/ER-ligated samarium(II) complexes **1a–d** can not only polymerize but also copolymerize styrene and ethylene. Of particular interest is that the copolymer products obtained under the coexistence of both monomers are styrene–ethylene block-copolymers as confirmed by NMR spectroscopic studies [17]. The thiolate complex **1c** is particularly useful for this copolymerization, which produces block styrene–ethylene copolymers with selectivity of higher than 90% (runs 6–9, Table 3). The styrene content in the copolymer products increased as the feeding amount of styrene monomer was increased under an atmosphere of ethylene, and could therefore be easily controlled (runs 2–9, Table 3).

The selective formation of block ethylene–styrene copolymers in the present reactions are in sharp contrast with what has been previously observed in group 4 metal-catalyzed reactions, in which random or alternating ethylene–styrene copolymers were always obtained under the coexistence of both monomers [19–33].[3] The present reactions are also in sharp contrast with those promoted by samarocene(II) complexes such as $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Sm(THF)_2$, in which the maximum incorporation of styrene into polyethylene was only two molecules per chain due to the steric hindrance of the bulky bis(pentamethylcyclopentadienyl) ligand set $(C_5Me_5)_2$ [9]. In

Table 3
Block copolymerization of ethylene and styrene by samarium(II) complexes bearing mixed C_5Me_5/ER ligands[a]

Run	Cat	Styrene (ml)	Yield (g)			Ps cont (mol%)[b]	M_n ($\times10^{-4}$)[c]	M_w/M_n[c]
			THF-sol (PS)[d]	Tol-sol (<108°C) (PES)[d]	Tol-insol (108°C) (PE)[d]			
1	**1a**	5	0.10	1.60	Trace	38	7.8	2.36
2	**1b**	3	0.46	2.14	Trace	34	15.9	1.97
3	**1b**	5	1.29	2.83	Trace	48	14.6	1.82
4	**1b**	7	1.37	2.94	Trace	68	15.1	1.92
5	**1b**	10	2.40	3.99	Trace	81	13.1	1.84
6	**1c**	3	0.06	1.31	Trace	13	11.3	2.21
7	**1c**	5	0.23	2.55	Trace	37	10.7	2.01
8	**1c**	7	0.27	2.74	Trace	43	13.7	1.73
9	**1c**	10	0.34	2.82	Trace	60	14.6	1.66
10	**1d**	3	1.89	1.21	Trace	36	5.7	3.75
11	**1e**	5	4.55	Trace	Trace	–	–	–

[a] Conditions: a precatalyst, 0.05 mmol; ethylene, 1 atm; total volume of styrene and toluene, 25 ml; room temperature, 30 min, unless otherwise noted.

[b] Polystyrene content in the copolymers determined by ^{13}C NMR in *ortho*-dichlorobenzene/$CDCl_2CDCl_2$ at 125°C.

[c] Determined at 135°C against polystyrene standard by GPC.

[d] PS, atactic polystyrene; PES, block ethylene–styrene copolymer; PE, polyethylene.

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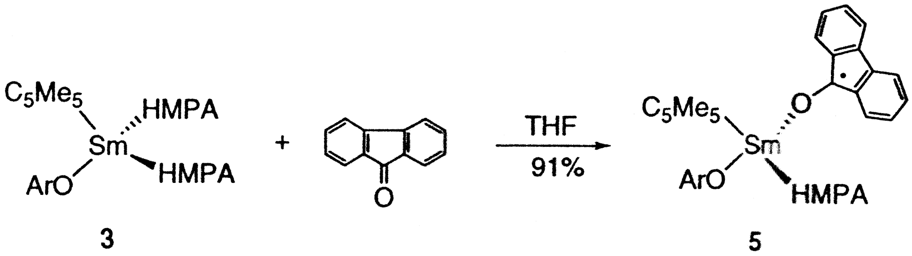
[2] It is well known that Yb(II) is less reducing than Sm(II), cf. $E_o(Sm^{3+}/Sm^{2+}) = -1.55$ V, $E_o(Yb^{3+}/Yb^{2+}) = -1.15$ V in aqueous medium.

[3] For examples of group 4 metal-catalyzed random or alternating copolymerization of ethylene with styrene (see Refs. [19–33]).



Scheme 5.

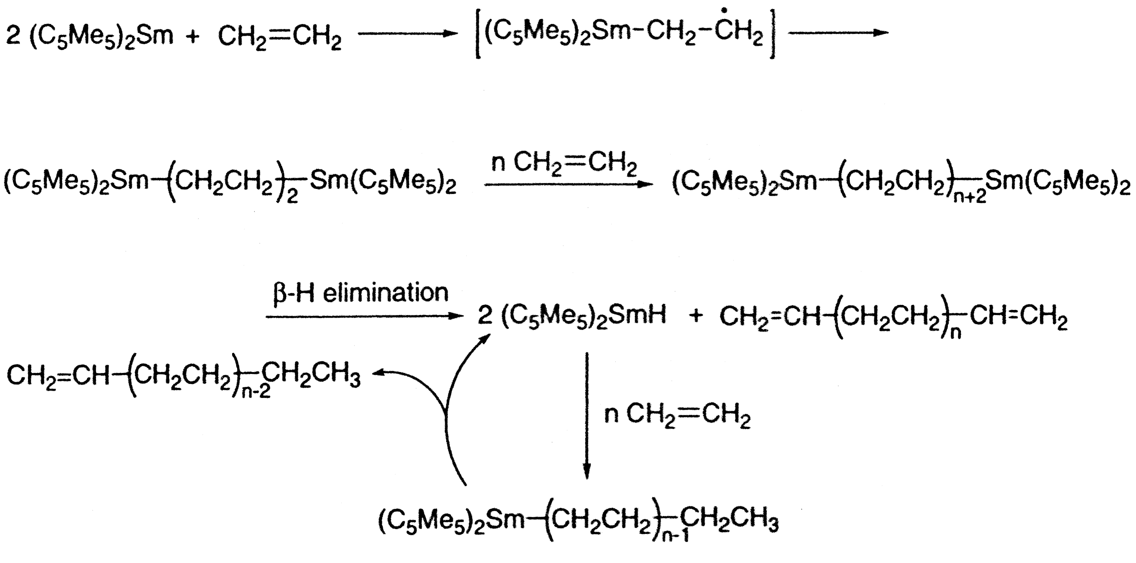
separate experiments it was established that $Sm(ER)_2$, KC_5Me_5, or KER are not active for the copolymerization of ethylene with styrene under the same conditions. These results strongly suggest that the heteroleptic '$(C_5Me_5)Sm(ER)$' unit in **1a–d** plays a very important role in the present copolymerization reactions.

In the case of complexes **2** and **3** the lack of activity for the polymerization reactions is probably due to the stable μ-OAr bridging in **2** and the strong coordination of the HMPA ligands in **3** [34,35], which prevent access of an olefin monomer to the metal center. In fact, when a more reactive electrophile, 9-fluorenone, was allowed to react with **3**, the C_5Me_5/OAr-ligated samarium(III) ketyl complex **5** was isolated in 91% yield (Scheme 5) [36], which well demonstrates that the mixed C_5Me_5/OAr ligand system is indeed able to stabilize both Sm(II) and Sm(III) species.

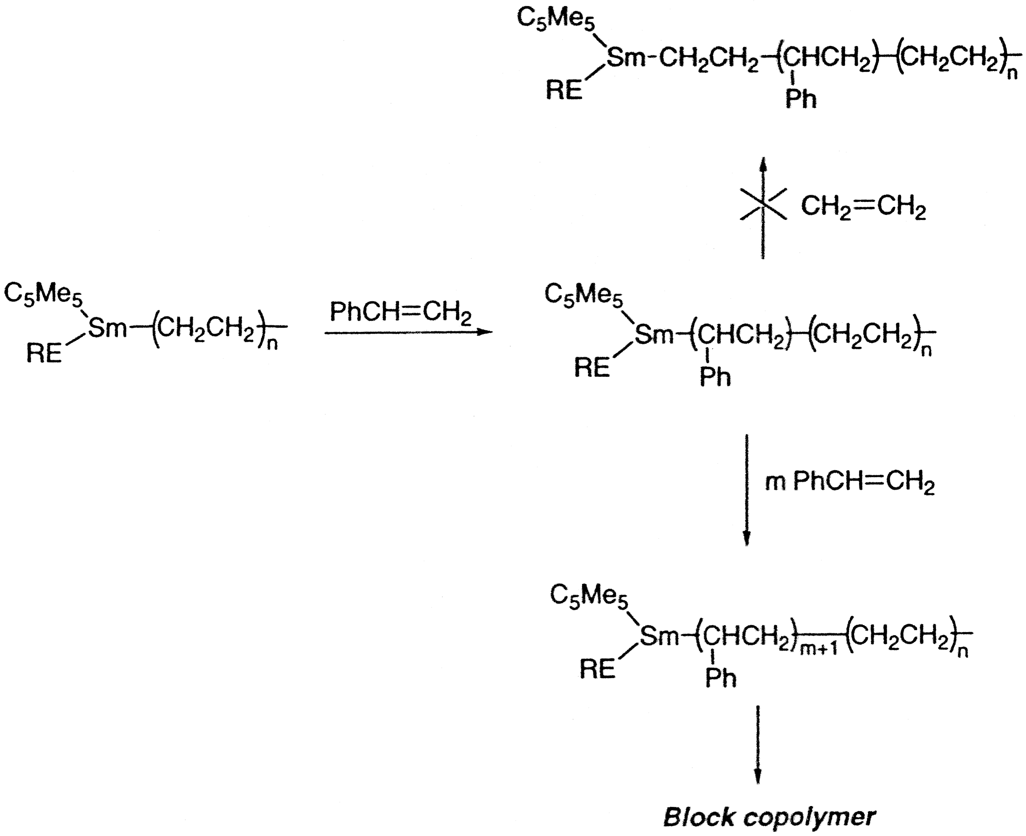
6. Mechanistic consideration on the polymerization reactions by C_5Me_5/ER-ligated Sm(II) complexes

As shown in Tables 1–3, dependence of the polymerization reaction on the ER ligands in **1a–e** has been observed in all cases, which strongly suggests that bonding interaction between an ER ligand and the samarium metal remains in a catalytic species during the polymerization reaction. The formation of a yellow solution at the beginning of the reactions and the narrow molecular weight distribution of the resulting polymers are consistent with the fact that the active species in the present polymerization reactions is a homogeneous Sm(III) species.

It is well known that the samarocene(II) complexes $(C_5Me_5)_2Sm(THF)_n$ ($n=0$, 2) can reductively dimerize ethylene to produce the corresponding Sm(III) species $(C_5Me_5)_2Sm(CH_2CH_2)_2Sm(C_5Me_5)_2$ which is active for polymerization (Scheme 6) [9,10,37]. In the present systems, similar Sm(III) species which are ligated by the heteroleptic C_5Me_5/ER ligands could be formed (Scheme 7). The more open ligand sphere provided by the C_5Me_5/ER ligand set could explain why the present systems are more active than the corresponding metallocene complexes. The selective formation of block ethylene–styrene copolymers in the present systems strongly suggests that the reactivity of the propagation center of polyethylene unit is critically different from that of polystyrene unit, one being able to incorporate both ethylene and styrene, while the other only the identical monomer. The nature of the metals and the ancillary ligands seem to be an important factor in determining the behavior of the propagation



Scheme 6.



Scheme 7.

centers. In the present cases, we tentatively assume that the propagation center of the polystyrene unit has some extent of anionic character which could prevent insertion of ethylene monomer, and thus the copolymerization reaction might probably be initiated by polymerization of ethylene followed by incorporation of styrene (Scheme 7). The ER ligand dependence of the copolymerization reactions and the relatively narrow molecular weight distributions of the resulting copolymers exclude the possibility that the copolymerization process is a radical reaction.

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