



Developments of rare earth metal catalysts for olefin polymerization

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Abstract

This review article describes recent developments in rare earth metal complexes as polymerization catalysts, focusing on the polymerization of ethylene and α -olefins. Most of this kind of catalysts had been based on metallocene type complexes, and their catalytic behaviors are surveyed. Advanced series of half-metallocene and non-Cp type catalyst systems are also summarized. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Rare earth metal complexes show unique reactivities due to their intermediate characters between transition metals and major group metals such as alkali and alkaline earth metals. Rare earth metals have high energy d orbitals, while their electron negativities are close to those of lithium and magnesium. As a consequence, M–C bonds are significantly polarized in rare earth complexes. In view of polymerization catalysis, these metals are potentially active for both coordination polymerization and ionic polymerization. Actually, block copolymerizations of olefins and polar monomers have been realized by using rare earth catalysts. Resulting copolymers could potentially be utilized as unique compatibilizers. Owing to those unique characteristics, organo-rare earth complexes are of great interests not only in the field of pure organometallic chemistry but also as polymerization catalysts [1–5].

The application of rare earth metals to olefin polymerization catalysts started with metallocene type complexes. The early studies revealed potential high activity of rare earth metallocene complexes for ethyl-

ene polymerization without cocatalysts. This is in sharp contrast to the fact that Group 4 metallocene catalysts require excess of cocatalysts such as methylaluminoxane (MAO). First block copolymerization of ethylene with polar monomers was achieved by using metallocene type rare earth complexes. Half metallocene type rare earth complexes have also been studied in parallel with metallocene type complexes. On the other hand, rare earth complexes without cyclopentadienyl (Cp) type ligands have been making a big progress in these three or four years, several systems showed high activities comparable to those of Group 4 metallocene catalysts.

In this article, we overview recent developments on polymerization catalysts based on rare earth metal complexes, especially focusing on the polymerization of ethylene and α -olefins.

2. Bis(cyclopentadienyl) type complexes

Neutral metallocene type complexes of Group 3 metals revealed active homogeneous ethylene polymerization catalysts. Representative results of the polymerization of ethylene by rare earth complexes are summarized in Table 1.

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Table 1
Ethylene polymerization activity of metallocene type complexes of rare earth metals

Complexes	Temperature (°C)	Activity ^a	$M_n/10^3$	M_w/M_n	T_m (°C)	References
[(C ₅ H ₅) ₂ ErMe] ₂ (1)	100	10.3	14	2.3	–	[6]
[(C ₅ H ₄ Me) ₂ ErMe] ₂ (2)	100	27.1	4.7	2.5	–	[6]
[(C ₅ H ₄ SiMe ₃) ₂ ErMe] ₂ (3)	100	82.3	1.5	2.5	–	[6]
[(C ₅ H ₄ SiMe ₃) ₂ YMe] ₂ (4)	100	16.6	2.1	2.1	–	[6]
[(C ₅ H ₄ SiMe ₃) ₂ YMe ₂ AlMe ₂] ₂ (5)	100	23.8	1.7	1.5	–	[6]
[(C ₅ Me ₄ Et) ₂ YBu ⁿ] ₂ (6)	100	42.3	6.8	2.7	–	[6]
[Cp [*] ₂ LaH] ₂ (7)	25	182000	680	2.03	–	[7]
[Cp [*] ₂ NdH] ₂ (8)	25	137000	590	1.81	–	[7]
[Cp [*] ₂ LuH] ₂ (9)	25	10000	96	1.37	–	[7]
Cp [*] ₂ LuMe (10)	50	6900	–	–	–	[1]
Cp [*] ₂ Nd(μ-Cl) ₂ Li(OEt ₂) ₂ (11)/Bu ₂ Mg (Mg/Nd = 20)	50	47000	–	–	–	[18]
[Me ₂ Si(C ₅ Me ₄) ₂ NdH] ₂ (12)	25	162	–	–	–	[24]
[{Me ₂ Si(C ₅ H ₃ SiMe ₃) ₂ } ₂ Sm ₂ H ₂ (THF) ₂] (16)	0–40	27	30–50	1.63–1.68	–	[26]
C ₁ -[Me ₂ Si{C ₅ H ₂ (SiMe ₃) ₂ } ₂ Sm]{CH(SiMe ₃) ₂ } (18)	23	30.8	99.6	1.84	–	[27]
C ₁ -[Me ₂ Si{C ₅ H ₂ (SiMe ₃) ₂ } ₂ Y]{CH(SiMe ₃) ₂ } (21)	23	186	331	1.65	–	[27]
<i>rac</i> -[Me ₂ Si{C ₅ H ₂ (SiMe ₃)(Bu ⁿ) ₂ } ₂ Sm](THF) ₂ (24)	23	139	360	1.60	–	[32]
<i>rac</i> -[Me ₂ Si{C ₅ H ₂ (SiMe ₃) ₂ } ₂ Sm](THF) (25)	23	30.2	131	3.54	–	[32]
C ₁ -[Me ₂ Si{C ₅ H ₂ (SiMe ₃) ₂ } ₂ Sm](THF) ₃ (26)	23	15.7	1000	1.60	–	[32]
<i>meso</i> -{(Me ₂ Si)(Me ₂ SiOSiMe ₂)(C ₅ H ₂ Bu ⁿ) ₂ } ₂ Sm(THF) ₂ (27)	23	470	47.3	3.49	–	[32]
C _{2v} -[Ph ₂ Si{C ₅ H ₂ (SiMe ₃) ₂ } ₂ Sm](THF) (28)	23	104	160	1.84	–	[32]
C _{2v} -{(Me ₂ SiOSiMe ₂) ₂ (C ₅ H ₂ Bu ⁿ) ₂ } ₂ Sm(THF) ₂ (29)	23	0.13	429	3.04	–	[32]

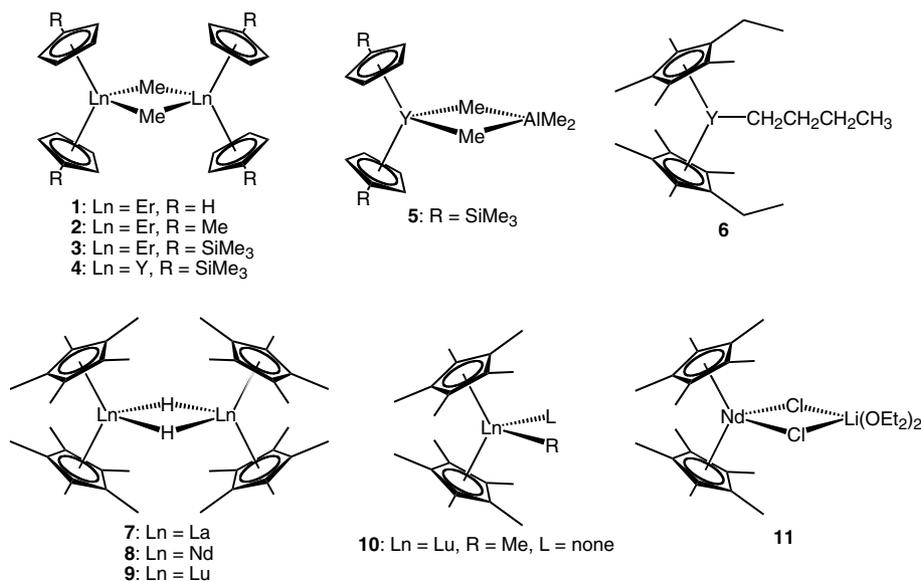
^a Activity: kg(mol of catalyst)⁻¹ h⁻¹ atm⁻¹.

2.1. Trivalent complexes

Trivalent metallocene complexes of rare earth metals (Scheme 1) are relatively stable, and therefore they are explored at first. In an early study of metallocenes **1–6**, sterically less bulky complexes having unsubstituted or mono(methyl)cyclopentadienyl ligands are thermally unstable, their life time for ethylene polymerization are less than 100 min at 100 °C [6]. The use of bulky ligands such as C₅Me₄Et and C₅Me₅ (Cp^{*}) provides relatively thermally stable and highly active ethylene polymerization cata-

lysts of rare earth metals [7–13]. The activities of bis-Cp^{*} hydride complexes are in the order of La (**7**) ≈ Nd (**8**) ≫ Lu (**9**) [7,14], with increasing metal size the activities tend to increase. The early lanthanide metallocene hydrides are more active than those of homogeneous Group 4 metallocene catalysts at the initial stage of the polymerization. A lutetium hydride complex, Cp^{*}₂LuH (**10**) polymerizes ethylene to produce polyethylene with narrow molecular weight distribution ($M_w/M_n = 1.37$) [7].

In contrast to the polymerization of ethylene, the reaction of Cp^{*}₂LnR (Ln = rare earth metal; R = alkyl,



Scheme 1.

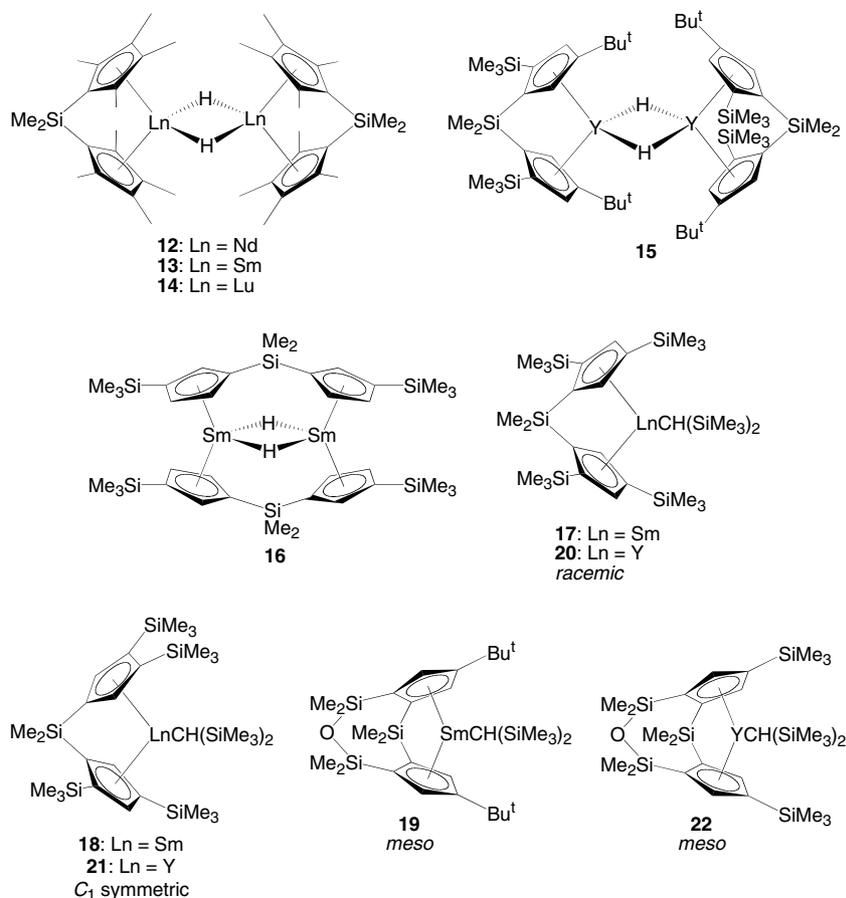
H) with propylene gives no polypropylene but affords an allyl complex, $\text{Cp}_2^*\text{Ln}(\eta^3\text{-allyl})$, via σ -bond metathesis reaction [7,14]. One molecule of propylene inserts into Lu–Me bond of Cp_2^*LuMe to form a corresponding isobutylene complex, $\text{Cp}_2^*\text{Lu}(\text{CH}_2\text{CHMe}_2)$ [1]. The successive insertion of propylene is three orders of magnitude slower than the first insertion. An yttrium complex, $[(\text{C}_5\text{H}_4\text{Me})_2\text{YH}(\text{THF})_2]$, reacts with ethylene and propylene to give $(\text{C}_5\text{H}_4\text{Me})_2\text{YR}(\text{THF})$ (R = ethyl, *n*-propyl) without polymerization [15]. A hydridoscandium complex, Cp_2^*ScH , also polymerizes ethylene, but does not polymerize propylene and isobutene [16]. Bis{1,3-bis(trimethylsilyl)cyclopentadienyl} complexes show similar activity with that of the corresponding Cp^* complexes [17].

Although bis- Cp^* type complexes of lanthanide elements are highly active for ethylene polymerization, the active species are still thermally unstable. A solution to this problem is the use of multi-component catalyst system. A chloride complex, $\text{Cp}_2^*\text{Nd}(\mu\text{-Cl})_2\text{Li}(\text{OEt}_2)_2$ (**11**), can be activated with alkylating reagents to form alkyl species in situ [18]. Dialkylmagnesium such as Bu_2Mg is the most useful activator. When 20 equiv. of Bu_2Mg was used, the catalyst system shows high and

constant activities for ethylene polymerization. Alkyl-lithium such as *n*-BuLi can also activate **11** to show high activity at the early stage of the polymerization, however, the activity rapidly decreases with time. Alkylaluminum such as Et_3Al is not effective for activation of **11**.

These metallocene type complexes can polymerize polar monomers as well as ethylene, e.g. the polymerization of methyl methacrylate (MMA) by Cp_2^*LnR affords highly syndiotactic poly(MMA) with narrow molecular distributions [19,20], and living polymerization of lactones are promoted by these complexes [21]. Thus, block copolymerization of ethylene with such polar monomers was achieved by using these rare earth complexes for the first time [22].

Although bulky Cp_2^*LnR type complexes are highly active for ethylene polymerization, they cannot polymerize 1-olefins (vide supra). A two component system, $\text{Cp}_2^*\text{Nd}(\mu\text{-Cl})_2\text{Li}(\text{OEt}_2)_2$ (**11**)/ BuEtMg , was reported to polymerize styrene, but the reaction mechanism is yet not clear [23]. In order to improve reactivities of rare earth catalysts toward 1-olefins, a series of *ansa*-metallocene type complexes have been studied (Scheme 2). Marks and co-workers [24] reported the co-polymerization of



Scheme 2.

ethylene with 1-hexene by using *ansa*-type complexes of lanthanide metals (**12–14**). More recently, bulky alkyl substituted *ansa*-type metallocene complexes of yttrium were reported to exhibit high activity for the polymerization of 1-hexene [2,11,25]. A chiral, C_2 -symmetric *ansa*-metallocene complex of yttrium, [*rac*-Me₂Si(C₅H₂-SiMe₃-2-Bu^t-4)₂YH]₂ (**15**), polymerizes propylene, 1-butene, 1-pentene, and 1-hexene slowly over a period of several days at 25 °C to afford isotactic polymers with modest molecular weight [11].

Hydrogenation of a similar samarium complex, *rac*-Me₂Si(C₅H₃SiMe₃-3)₂Sm{CH(SiMe₃)₂}(THF) afforded a binuclear complex, [{Me₂Si(C₅H₃SiMe₃-3)₂Sm₂H₂-(THF)₂] (**16**), in which the linked Cp ligands are bridging between two samarium atoms [26]. The complex **16** shows moderate activity for ethylene polymerization and for copolymerization of ethylene with polar monomers. A series of *rac*-, C_1 -, and *meso* complexes of samarium and yttrium **17–22** was synthesized and only the C_1 -complexes **18** and **21** showed ethylene polymerization activity [27]. In addition, the yttrium complex **22** polymerized α -olefins such as 1-pentene and 1-hexene as well as ethylene. Although its activity was very low, the poly(1-hexene) obtained at 0 °C had high molecular weight ($M_n = 64500$) and narrow molecular weight distribution ($M_w/M_n = 1.20$). This type of *ansa*-metallocene complexes were effective catalysts for the block copolymerization of polar monomers not only with ethylene but also with α -olefins [28].

A three component system based on a *ansa*-metallocene complex, {Me₂Si(C₅H₃SiMe₃-3)₂}NdCl/BuLi/AlHBU₂ⁱ, is an efficient catalyst for the copolymerization of ethylene and butadiene [29]. The butadiene contents

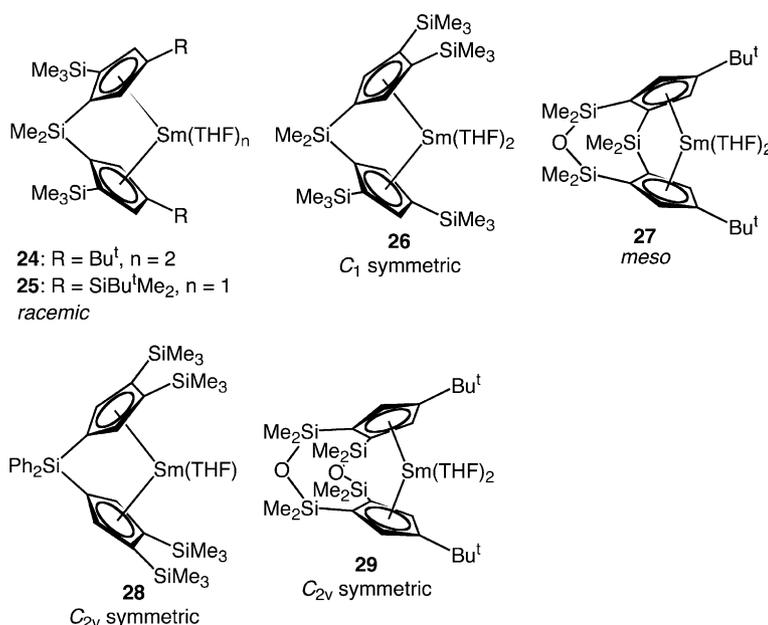
of the copolymers can be controlled in a range of 5–63%, and the poly(butadiene) segments has 1,4-*trans* structure. The resulting copolymers have an alternating character. With increasing butadiene contents of the copolymers, their melting points drop.

2.2. Divalent complexes

Several divalent lanthanide ions such as Sm²⁺, Eu²⁺, and Yb²⁺ are stable and are reducing agents. The reducing powers of these divalent lanthanides are in an order of Sm²⁺ > Yb²⁺ \gg Eu²⁺ [30]. Thus, Sm²⁺ is an especially strong reducing agent among them, and are potentially active for olefin polymerization to initiate the polymerization by bimetallic two electron reduction of the monomer, in which the divalent metal center is oxidized to trivalent.

Divalent samarium complexes, Cp₂^{*}Sm and Cp₂^{*}Sm(THF)₂ (**23**), was reported to show high activity for ethylene polymerization [14] to give polymers with relatively low molecular weight. These complexes reacts with 1-olefins to form stable π -allyl complexes [14,31].

Recently, a series of divalent *ansa*-type samarocene complexes **24–29** was shown to catalyze not only homopolymerization of ethylene but also block copolymerization of α -olefins and polar monomers (Scheme 3) [32]. In the homopolymerization of ethylene, the activities of these complexes were in order of *meso* **27** > *rac* **24** > C_{2v} **28** > *rac* **25** > C_1 **26** \gg C_{2v} **29**. In sharp contrast of the high activity of *meso* **27** for ethylene polymerization, only the racemic complexes **24** and **25** were active for α -olefin polymerizations among these complexes. Although the activities of these complexes were



Scheme 3.

rather low ($\sim 0.3 \text{ kg}(\text{mol of catalyst})^{-1} \text{ h}^{-1}$), both complexes gave highly isotactic polymers. The divalent *rac* and *meso* complexes promoted ABA-type triblock copolymerization of ethylene with polar monomers such as MMA and ϵ -caprolactone [33]. The *rac* complex **24** should enable triblock copolymerization of α -olefins and polar monomers.

3. Mono(cyclopentadienyl) type complexes

Several half-metallocene type complexes have been reported to show catalytic activities for olefin polymerization. Representative results of ethylene polymerization are summarized in Table 2.

Cationic alkyl species of Group 4 metals having linked Cp-amide type ligands, e.g. $[(\text{C}_5\text{Me}_4\text{SiMe}_2\text{NBu}^+)\text{Ti}(\text{alkyl})]^+$, are known for their excellent activity and copolymerizability of olefins [34]. A series of Cp-amide complexes of rare earth metals have also been studied (Scheme 4). In contrast to the titanium catalysts, the corresponding neutral Cp-amide type complexes of scandium, $[(\text{C}_5\text{Me}_4\text{SiMe}_2\text{NBu}^+)\text{ScH}(\text{PMe}_3)]_2$ (**30**), polymerizes not only ethylene but also α -olefins such as propylene, 1-butene, and 1-pentene, although its activity is very low [12,35]. The corresponding yttrium alkyl and hydride complexes, $(\text{C}_5\text{Me}_4\text{SiMe}_2\text{NBu}^+)\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})$ (**31**) and $[(\text{C}_5\text{Me}_4\text{SiMe}_2\text{NBu}^+)\text{YH}(\text{THF})]_2$ (**32**), also shows low activities for ethylene polymerization to give linear polyethylene [36]. A *n*-hexyl derivative, $[(\text{C}_5\text{Me}_4\text{SiMe}_2\text{NBu}^+)\text{Y}(\text{C}_6\text{H}_{13})](\text{THF})_2$ (**33**), are effective for styrene polymerization to give syndiotactic-enriched polymers with narrow molecular weight distributions. A recent patent reported cationic alkyl species of scandium having Cp-amine ligands,

$[(\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{NMe}_2)\text{Sc}(\text{alkyl})]^+$, are effective for catalytic olefin polymerization [37]. A divalent samarium complex with a linked Cp-amide type ligand, $\{(\text{C}_5\text{Me}_4)\text{SiMe}_2\text{NPh}\}\text{Sm}(\text{THF})$ (**34**), shows moderate activity for ethylene polymerization to yield polyethylene with high molecular weight and narrow molecular weight distribution, while the corresponding ytterbium(II) complex **35** is inactive [38]. The corresponding linked Cp-phosphido complex, $\{(\text{C}_5\text{Me}_4)\text{SiMe}_2\text{P}(\text{C}_6\text{H}_2\text{Bu}^t\text{-2, 4, 6})\}\text{Sm}(\text{THF})$ (**36**), is less active than **34** but produces extremely high molecular weight polyethylene [39].

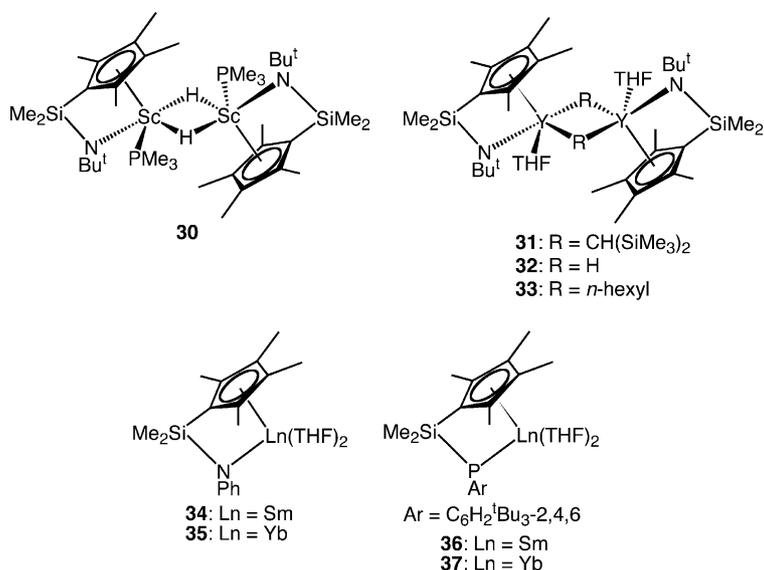
An aryloxo(hydrido) complex of yttrium, $\{\text{Cp}^*\text{Y}(\text{OC}_6\text{H}_3\text{Bu}^t\text{-2,6})(\mu\text{-H})\}_2$ (**38**) (Scheme 5), shows very low activity for ethylene polymerization [40]. A dialkyl lanthanum complex, $\text{Cp}^*\text{La}\{\text{CH}(\text{SiMe}_3)_2\}_2(\text{THF})$ (**39**) (Scheme 5), shows moderate activity for ethylene polymerization [41]. It is notable that the resulting polyethylene has significantly narrow molecular weight distribution and the molecular weight of the polymer increases with time, indicating living character of the polymerization system. The complex **39** is also active for the polymerizations of styrene, MMA, hexyl isocyanate, and acrylonitrile. Block copolymerization of ethylene and MMA can be promoted by **39** as is the case of metallocene complexes.

Recently, unique divalent lanthanide complexes having Cp^*M ($\text{M} = \text{K}, \text{Na}$) as a neutral ligand have been reported. In this series of complexes, Cp^*M can be regarded as a leaving group, and thus those complexes can be categorized into mono-Cp type catalysts (Scheme 6). The reaction of $\text{Cp}_2^*\text{Ln}(\text{THF})_2$ ($\text{Ln} = \text{Sm}, \text{Yb}$) with KER ($\text{ER} = \text{aryloxo}, \text{thiolate}, \text{amide}, \text{and phosphide}$) in THF affords a series of polymeric divalent lanthanide complexes, $[\text{Cp}^*\text{Ln}(\text{THF})_x(\text{ER})\text{Cp}^*\text{K}(\text{THF})_y]_n$ (**40–46**) [42]. The use of sodium amide instead of potassium

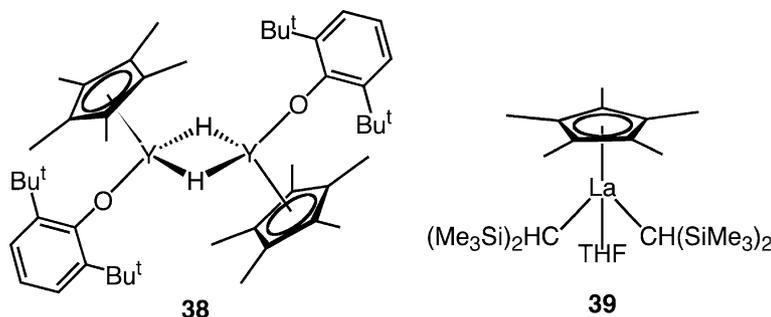
Table 2
Ethylene polymerization activities of half-metallocene type complexes of rare earth metals for ethylene polymerization

Complex	Temperature (°C)	Activity ^a	$M_n/10^3$	M_w/M_n	T_m (°C)	References
$\{(\text{C}_5\text{Me}_4)\text{SiMe}_2\text{NBu}^+\text{Y}(\text{H}_2\text{SiMe}_3)(\text{THF})\}$ (31)	r.t.	0.21	–	–	136	[36]
$\{[(\text{C}_5\text{Me}_4)\text{SiMe}_2\text{NBu}^+\text{YH}(\text{THF})]_2\}$ (32)	r.t.	0.08	–	–	136	[36]
$\{(\text{C}_5\text{Me}_4)\text{SiMe}_2\text{NPh}\}\text{Sm}(\text{THF})$ (34)	25	44.8	726	1.58	–	[38]
$\{(\text{C}_5\text{Me}_4)\text{SiMe}_2\text{P}(\text{C}_6\text{H}_2\text{Bu}^t\text{-2, 4, 6})\}\text{Sm}(\text{THF})$ (36)	25	13.6	>4000	–	–	[39]
$\{\text{Cp}^*\text{Y}(\text{OC}_6\text{H}_3\text{Bu}^t\text{-2,6})(\mu\text{-H})\}_2$ (38)	25	0.34	12	10.8	–	[40]
$\text{Cp}^*\text{La}\{\text{CH}(\text{SiMe}_3)_2\}_2(\text{THF})$ (39)	25	23.4	145	1.28	–	[41]
$[\text{Cp}^*\text{Sm}(\text{OC}_6\text{H}_2\text{Bu}^t\text{-2, 6-Me-4})\text{Cp}^*\text{K}(\text{THF})_2]_n$ (40)	25	194	434	2.22	–	[42]
$[\text{Cp}^*\text{Sm}(\text{OC}_6\text{H}_3\text{Pr}_2^i\text{-2, 6})\text{Cp}^*\text{K}(\text{THF})_n]$ (41')	25	120	330	2.49	–	[42]
$[\text{Cp}^*\text{Sm}(\text{SC}_6\text{H}_2\text{Pr}_2^i\text{-2, 4, 6})\text{Cp}^*\text{K}(\text{THF})_n]$ (42')	25	119	580	1.79	–	[42]
$[\text{Cp}^*\text{Sm}(\text{NHC}_6\text{H}_2\text{Bu}^t\text{-2, 4, 6})\text{Cp}^*\text{K}(\text{THF})_2]_n$ (43)	25	57.6	497	2.90	–	[42]
$[\text{Cp}^*\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}\text{Cp}^*\text{K}(\text{THF})_2]_n$ (44)	25	22.0	3099	2.83	–	[42]
$[\text{Cp}^*\text{Sm}(\text{THF})(\text{PHC}_6\text{H}_2\text{Bu}^t\text{-2, 4, 6})\text{K}(\text{THF})\text{Cp}^*]_n$ (46)	25	163	818	1.64	–	[42]
$\text{Cp}^*\text{Sm}\{\text{N}(\text{SiMe}_3)_2\}\text{Cp}^*\text{Na}(\text{THF})$ (47)	25	46.0	865	2.30	–	[42]
$[\text{Cp}^*\text{Sm}\{\text{CH}(\text{SiMe}_3)_2\}\text{Cp}^*\text{K}(\text{THF})_2]_n$ (49)	25	264	1400	1.62	–	[43]
$[\text{Cp}^*\text{Sm}(\text{SiH}_3)(\text{THF})\text{Cp}^*\text{K}(\text{THF})_n]$ (52)	25	94	113	3.51	–	[43]
$[\text{Cp}^*\text{Eu}(\text{SiH}_3)(\text{THF})\text{Cp}^*\text{K}(\text{THF})_n]$ (53)	25	75	390	1.94	–	[43]
$[\text{Cp}^*\text{Yb}(\text{SiH}_3)(\text{THF})\text{Cp}^*\text{K}(\text{THF})_n]$ (54)	25	9	108	3.39	–	[43]

^a Activity: $\text{kg}(\text{mol of catalyst})^{-1} \text{ h}^{-1} \text{ atm}^{-1}$.



Scheme 4.



Scheme 5.

amide gave discrete complexes, Cp*Ln{N(SiMe₃)₂}Cp*-Na(THF)₃ (Ln = Sm (**47**), Yb (**48**)). These samarium complexes show moderate activities for the polymerization of ethylene, in contrast to the low activity of a neutral mono-Cp* aryloxoyttrium hydride complex (**38**) [40]. The activities are higher than Cp₂Sm(THF)₂ indicating that Cp*M (M = K, Na) are better leaving group than THF. The ytterbium complexes do not polymerize ethylene due to their low reducing power. These samarium complexes are also active for the polymerization of styrene, while Cp₂Sm(THF)₂ is inactive for styrene polymerization. Furthermore, these complexes enable the block copolymerization of ethylene with styrene.

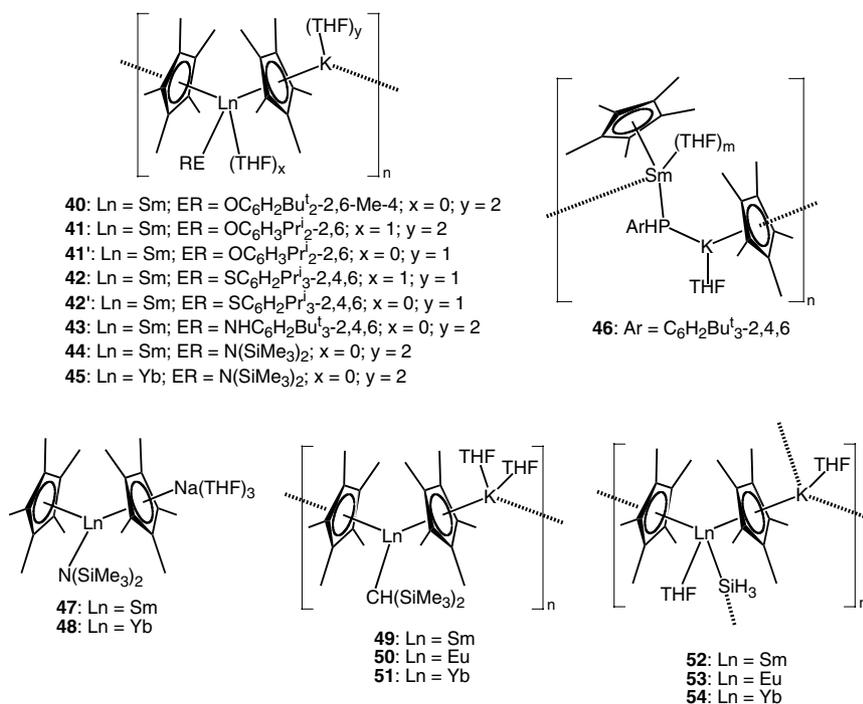
Cp₂Ln(THF)₂ (Ln = Sm, Eu, Yb) also react with KCH(SiMe₃)₂ in THF to afford divalent alkyl complexes, [Cp*Ln{CH(SiMe₃)₂}Cp*K(THF)₂]_n (Ln = Sm (**49**), Eu (**50**), Yb (**51**)) [43]. The samarium complex **49** shows high activity for the polymerization of ethylene and styrene. The polymerization should initiate through one electron transfer from Sm²⁺ to the monomer. The corresponding europium and ytterbium complexes are almost inactive due to their low reducing power. In con-

trast, all the three analogous silyl complexes of divalent lanthanides, [Cp*Ln(SiH₃)(THF)Cp*K(THF)]_n (Ln = Sm (**52**), Eu (**53**), Yb (**54**)), showed high activities for the polymerization of ethylene and styrene [43]. In these systems, the polymerization could be initiated by migratory addition of the SiH₃ to the monomer.

4. Cp-free complexes

Although Cp-free rare earth catalysts for olefin polymerization had been very few until year 2000, highly active Cp-free catalysts have been developing in these three or four years (Table 3, Scheme 7).

Early examples of Cp-free rare earth catalysts for ethylene polymerization are tris(pyrazolyl)borate complexes [44]. A series of tris(3,5-dimethyl-1-pyrazolyl)borohydride (Tp^{Me}) complexes of yttrium was synthesized and found to show activity for ethylene polymerization. Dialkyl complexes, Tp^{Me}YR₂(THF) (R = Ph, CH₂SiMe₃) were isolated from the reaction of Tp^{Me}YCl₂(THF) (**55**) with two equiv. of RLi. The **55**/



Scheme 6.

Table 3
Ethylene polymerization activities of rare earth metal complexes without Cp-type ligands

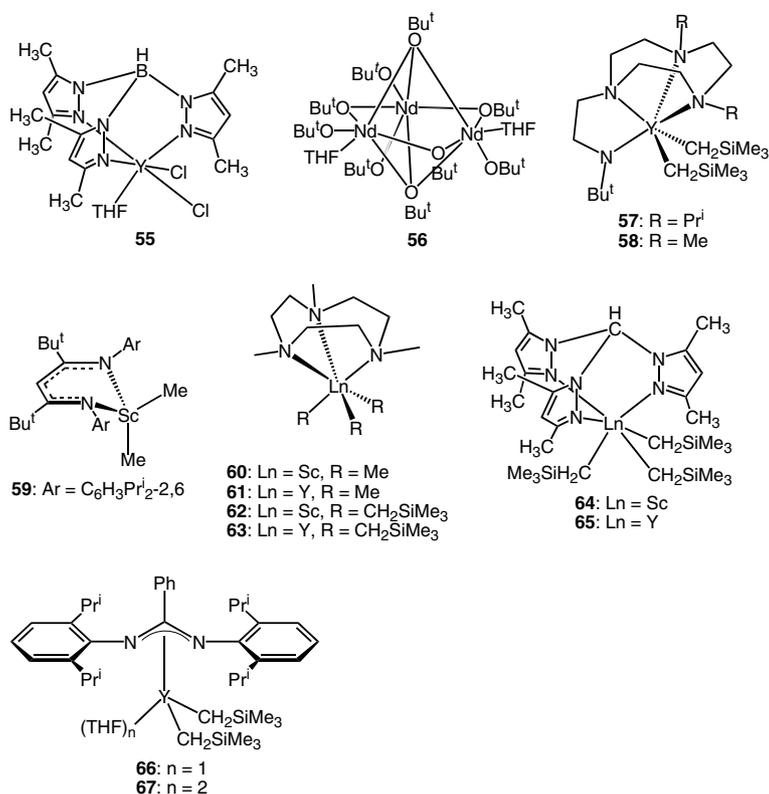
Complex	Temperature (°C)	Activity ^a	$M_n/10^3$	M_w/M_n	T_m (°C)	Reference
Tp ^{Me} YCl ₂ (THF) (55)/2RLi						
R = Me	25	0.02	–	–	142.3	[44]
R = Ph	25	0.63	100	2.50	142.3	[44]
R = CMe ₃	25	1.1	1200	4.14	142.3	[44]
R = CH ₂ SiMe ₃	25	0.08	–	–	142.3	[44]
R = CH ₂ SiMe ₃ + H ₂	25	5.1	1900	15.86	142.3	[44]
[Nd ₃ (μ ₃ -OBu ^t) ₂ (μ ₂ -OBu ^t) ₃ (OBu ^t) ₄ (THF) ₂] (56)/Mg(<i>n</i> -hex) ₂	0	10	30	2.3	139	[45]
[N,N'-Pr ⁱ ₂ -tacn-N''-(CH ₂) ₂ NBu ^t]Y(CH ₂ SiMe ₃) ₂ (57)/[PhNMe ₂ H][B(C ₆ F ₅) ₄] ^b	80	1790	98	6.0	–	[47]
[N,N'-Me ₂ -tacn-N''-(CH ₂) ₂ NBu ^t]Y(CH ₂ SiMe ₃) ₂ (58)/[PhNMe ₂ H][B(C ₆ F ₅) ₄] ^b	30	960	–	–	–	[47]
(Calix[6]arene)Nd/AlBu ^t ₃	80	3.3	931 ^c	–	135.5	[48]
(Nacnac)ScMe ₂ (59)/PMAO-IP	50	59	942	1.98	–	[49]
(Nacnac)ScMe ₂ (59)/B(C ₆ F ₅) ₃	50	1.5	618	1.7	–	[49]
(Me ₃ [9]aneN ₃)Sc(CH ₂ SiMe ₃) ₃ (62)/B(C ₆ F ₅) ₃	33	240	353	bimodal	–	[51]
(Me ₃ [9]aneN ₃)Y(CH ₂ SiMe ₃) ₃ (63)/B(C ₆ F ₅) ₃	33	10	1180	bimodal	–	[51]
{HC(Me ₂ pz) ₃ }Sc(CH ₂ SiMe ₃) ₃ (64)/B(C ₆ F ₅) ₃	33	290	192	bimodal	–	[51]
{HC(Me ₂ pz) ₃ }Y(CH ₂ SiMe ₃) ₃ (65)/B(C ₆ F ₅) ₃	33	0	–	–	–	[51]
{PhC(NAR) ₂ }Y(CH ₂ SiMe ₃) ₂ (THF) (66)/[PhNMe ₂ H][B(C ₆ F ₅) ₄]	50	1040	430	1.2	–	[57]
{PhC(NAR) ₂ }Y(CH ₂ SiMe ₃) ₂ (THF) ₂ (67)/[PhNMe ₂ H][B(C ₆ F ₅) ₄]/TIBAO	50	2670	361	2.1	–	[57]
Y(CH ₂ SiMe ₃) ₃ (THF) ₂ /[NMe ₂ HPh][B(C ₆ F ₅) ₄]/Al(CH ₂ SiMe ₃) ₃ (68)	25	1840	111	2.9	138	[58]

^a Activity: kg(mol of catalyst)⁻¹ h⁻¹ atm⁻¹.^b tacn = triazaclonane.^c M_n value.

2LiR systems conduct the polymerization of ethylene leading to linear high molecular weight polymers, although their activities were rather low.

In 2000, a neodymium *t*-butoxide complex, [Nd₃(μ₃-OBu^t)₂(μ₂-OBu^t)₃(OBu^t)₄(THF)₂] (**56**), was reported to show moderate activity for ethylene polymerization in the presence of one equivalent of dialkylmagnesium in toluene at 0 °C [45,46]. Progressive deactivation of the catalyst system was observed above 20 °C. The resulting

polymers do not contain unsaturated end groups, indicating pseudo living polymerization, although the molecular weight distributions of the polymers are rather broad. During the course of the polymerization, polymer-like precipitate appears in the reaction mixture. The precipitate is assumed to be a Nd-polyethylenyl compound, which still has activity for further ethylene polymerization and enables block copolymerization of ethylene with MMA [46].



Scheme 7.

As an analogue of CGC-type complexes of Group 4 metals, 1,4,7-triazacyclononane-amide complexes of yttrium, $[N, N'-R_2\text{-tacn-}N''\text{-(CH}_2)_2\text{NBu}^t]Y(\text{CH}_2\text{SiMe}_3)_2$ (**57**: R = Prⁱ, **58**: R = Me; tacn = triazacyclononane), were synthesized [47]. These complexes show high activities for ethylene polymerization upon activation with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$.

Calixarene complexes of rare earth metals exhibit moderate activity in the presence of AlBu_3^t , although their structures are not clear [48].

A dimethylscandium complex having a bulky β -diketiminate (Nacnac) ligand, $(\text{Nacnac})\text{ScMe}_2$ (**59**), reacts with one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ to form a cationic monomethyl complex, $[(\text{Nacnac})\text{ScMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$, whose structure has been determined by X-ray analysis [49]. The corresponding 1:0.5 reaction of **59** with $\text{B}(\text{C}_6\text{F}_5)_3$ gave a μ -methyl dimeric cation, while the 1:2 reaction afforded mononuclear dicationic complex. An *endo exo* diastereomeric interconversion of **59** was observed in solution. The complex **59** can also be activated with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, or PMAO-IP (a kind of MAO made by alcoholysis of AlMe_3) to show high ethylene polymerization activity.

Neutral trimethyl complexes having a triazacyclononane ligand, $(\text{Me}_3[9]\text{aneN}_3)\text{MMe}_3$ (**60**: Ln = Sc, **61**: Ln = Y), are unreactive toward olefin insertion as it is. In combination with ion-pair forming agents such as $\text{B}(\text{C}_6\text{F}_5)_3$ and $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$, the scandium

complex **60** polymerizes 1-pentene to give low molecular weight polymers [50]. The corresponding tris(trimethylsilylmethyl) complex **62** shows high activity for ethylene polymerization [51]. The yttrium derivative **63** is much less active than **62**. A cationic lanthanum complex is highly active for *cis*-selective alkyne dimerization [52].

A neutral version of the anionic tris(pyrazolyl)borate ligand, tris(pyrazolyl)methane, was adopted for trialkyl complexes of rare earth metals, $\{\text{HC}(\text{Me}_2\text{pz})_3\}\text{Ln}(\text{CH}_2\text{SiMe}_3)_3$ (**64**: Ln = Sc, **65**: Ln = Y) [51]. The scandium complex **64** effectively catalyzes ethylene polymerization upon activation with $\text{B}(\text{C}_6\text{F}_5)_3$, while the yttrium complex **65** is almost inactive.

As an alternative of Cp ligands, the use of benzamidinate ligands have been studied [53]. Several bis(benzamidinate) complexes of yttrium were reported to polymerize lactide [54,55], but they are not active for ethylene polymerization. The use of bulky ligands and bulky alkyl groups enabled to synthesize mono(benzamidinate) complexes of yttrium, $\{\text{PhC}(\text{NAr})_2\}\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_n$ (**66**: $n = 1$, **67**: $n = 2$; Ar = C₆H₃Prⁱ_{2,6}), can be prepared from the reaction of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ with $\{\text{PhC}(\text{NAr})_2\}\text{H}$, in which the number of the coordinated THF depends on the used solvent [57]. The mono-THF adduct **66** is highly active for ethylene polymerization in combination with

[PhNMe₂H][B(C₆F₅)₄] to give polyethylene with narrow molecular weight distribution. The molecular weights and the yields of the polymers increases with time, indicating living character of the polymerization system. In contrast, the bis-THF adduct **67** is inactive under the same reaction conditions, while **67** shows even higher activities than **66** in the presence of TIBAO (triisobutyl aluminoxane). The polymer obtained with **67**/[PhNMe₂H][B(C₆F₅)₄]/TIBAO had lower molecular weight and broader molecular weight distribution than those obtained with **66**/[PhNMe₂H][B(C₆F₅)₄].

Tris(alkyl) rare earth complexes, Ln(CH₂SiMe₃)₃(THF)₂ (Ln = Tm, Er, Y, Ho, Dy, Tb), had been reported to be effective as catalyst precursors for ethylene polymerization in combination with [NMe₂HPh][B(C₆F₅)₄] (B/Ln = 5) and alkylaluminum (Al/Y = 200) [58]. The use of larger metal tended to show higher activities. The activities are also dependent on the kind of alkylaluminum, and the highest activity was achieved by using Y(CH₂SiMe₃)₃(THF)₂/[NMe₂HPh][B(C₆F₅)₄]/Al(CH₂SiMe₃)₃ (**68**). To get information about the active species, some model reactions were performed. The reaction of Y(CH₂SiMe₃)₃(THF)₂ with three equiv. of [NMe₂HPh][BPh₄] in THF afforded a dicationic complex, [Y(CH₂SiMe₃)₃(THF)₅]²⁺[BPh₄]₂⁻. When a yttrium tris(aluminate), Y{(μ-Me)₂AlMe₂}₃, was treated with an excess of [NMe₂HPh][BPh₄] in THF, a dicationic complex, [YMe(THF)₆]²⁺[BPh₄]₂⁻, was also isolated. The reaction of Y(CH₂SiMe₃)₃(THF)₂ with equimolar Al(CH₂SiMe₃)₃ was found to form [Y(CH₂SiMe₃)₂(THF)_x]⁺[Al(CH₂SiMe₃)₄]⁻. When this monocationic complex was activated with [NMe₂HPh][B(C₆F₅)₄], similar activity with **68** was observed. From these observations, the active species in these systems were speculated to be dicationic species, [Ln(CH₂SiMe₃)(solvent)]₂²⁺.

5. Conclusion

Because of their high sensitivities to air and moisture, bulky metallocene type rare earth complexes had been mainly studied as olefin polymerization catalysts. Now, research interests seem to be moving from metallocene complexes onto half metallocene and non-Cp type complexes. One of keys to advance this sort of catalysts could be a use of an appropriate cocatalyst. Particularly, a combination of di- or trialkyl complexes with an ion pair-forming reagent such as [NMe₂HPh][B(C₆F₅)₄] could be a good strategy. Moreover, rare earth catalysts are potentially active not only for olefin polymerization but also for the polymerization of polar monomers. Development of practical rare earth catalysts for copolymerization of olefins with polar monomers should make a big impact on chemical industry, and we suppose it to be promising.

References

- [1] P.L. Watson, G.W. Parshall, *Acc. Chem. Res.* 18 (1985) 51.
- [2] H. Yasuda, E. Ihara, *Macromol. Chem. Phys.* 196 (1995) 2417.
- [3] H. Yasuda, E. Ihara, *Bull. Chem. Soc. Jpn.* 70 (1997) 1745.
- [4] Z. Hou, Y. Wakatsuki, *Coord. Chem. Rev.* 231 (2002) 1.
- [5] W.E. Piers, D.J.H. Emslie, *Coord. Chem. Rev.* 233-234 (2002) 131.
- [6] D.G.H. Ballard, A. Curtis, J. Holton, J. McMeeking, R. Pearce, *J. Chem. Soc., Chem. Commun.* (1978) 994.
- [7] G. Jeske, H. Lauke, H. Mauermann, P.N. Swepston, H. Schumann, T.J. Marks, *J. Am. Chem. Soc.* 107 (1985) 8091.
- [8] M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, *J. Am. Chem. Soc.* 109 (1987) 203.
- [9] B.J. Burger, M.E. Thompson, W.D. Cotter, J.E. Bercaw, *J. Am. Chem. Soc.* 112 (1990) 1566.
- [10] E. Bunel, B.J. Burger, J.E. Bercaw, *J. Am. Chem. Soc.* 110 (1988) 976.
- [11] E.B. Coughlin, J.E. Bercaw, *J. Am. Chem. Soc.* 114 (1992) 7606.
- [12] P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, *J. Am. Chem. Soc.* 116 (1994) 4623.
- [13] S. Hajela, J.E. Bercaw, *Organometallics* 13 (1994) 1147.
- [14] W.J. Evans, T.A. Ulibarri, J.W. Ziller, *J. Am. Chem. Soc.* 112 (1990) 2314.
- [15] W.J. Evans, J.H. Meadows, W.E. Hunter, J.L. Atwood, *J. Am. Chem. Soc.* 106 (1984) 1291.
- [16] M.E. Thompson, J.E. Bercaw, *Pure Appl. Chem.* 56 (1984) 1.
- [17] Y. Satoh, N. Ikitake, Y. Nakayama, S. Okuno, H. Yasuda, *J. Organomet. Chem.* 667 (2003) 42.
- [18] T.M. Pettijohn, H.L. Hsieh, *MetCon'93 Worldwide Metallocene Conference* (Houston, TX, USA), 1993, p. 97.
- [19] H. Yasuda, Y. Yamamoto, K. Yokota, S. Miyake, A. Nakamura, *J. Am. Chem. Soc.* 114 (1992) 4908.
- [20] H. Yasuda, H. Yamamoto, M. Yamashita, K. Yokota, A. Nakamura, S. Miyake, Y. Kai, N. Kanehisa, *Macromolecules* 26 (1993) 7134.
- [21] H. Yasuda, H. Yamamoto, Y. Takemoto, M. Yamashita, K. Yokota, S. Miyake, A. Nakamura, *Macromol. Chem., Macromol. Symp.* 67 (1993) 187.
- [22] H. Yasuda, M. Furo, H. Yamamoto, A. Nakamura, S. Miyake, N. Kibino, *Macromolecules* 25 (1992) 5115.
- [23] S. Bogaert, J.-F. Carpentier, T. Chenal, A. Mortreux, G. Ricart, *Macromol. Chem. Phys.* 201 (2000) 1813.
- [24] G. Jeske, L.E. Schock, P.N. Sweptson, H. Schumann, T.J. Marks, *J. Am. Chem. Soc.* 107 (1985) 8103.
- [25] H. Yasuda, E. Ihara, *Koubunshi* 43 (1994) 534.
- [26] G. Desurmont, Y. Li, H. Yasuda, T. Maruo, N. Kanehisa, Y. Kai, *Organometallics* 19 (2000) 1811.
- [27] E. Ihara, S. Yoshioka, M. Furo, K. Katsura, H. Yasuda, S. Mohri, N. Kanehisa, Y. Kai, *Organometallics* 20 (2001) 1752.
- [28] G. Desurmont, T. Tokimitsu, H. Yasuda, *Macromolecules* 33 (2000) 7679.
- [29] C. Boisson, V. Monteil, D. Ribour, R. Spitz, F. Barbotin, *Macromol. Chem. Phys.* 204 (2003) 1747.
- [30] H.B. Kagan, *New J. Chem.* 14 (1990) 453.
- [31] W.J. Evans, T.A. Ulibarri, J.W. Ziller, *J. Am. Chem. Soc.* 112 (1990) 219.
- [32] E. Ihara, M. Nodono, K. Katsura, Y. Adachi, H. Yasuda, M. Yamagashira, H. Hashimoto, N. Kanehisa, Y. Kai, *Organometallics* 17 (1998) 3945.
- [33] G. Desurmont, M. Tanaka, Y. Li, H. Yasuda, T. Tokimitsu, S. Tone, A. Yanagase, *J. Polym. Sci., Part A: Polym. Chem.* 38 (2000) 4095.
- [34] J. Scheirs, W. Kaminsky, John Wiley & Sons Ltd, West Sussex, 2000.

- [35] P.J. Shapiro, E. Bunel, W.P. Schaefer, J.E. Bercaw, *Organometallics* 9 (1990) 867.
- [36] K.C. Hultsch, P. Votch, K. Beckerle, T.P. Spaniol, J. Okuda, *Organometallics* 19 (2000) 228.
- [37] J.A.M. Canich, T.D. Schaffer, J.N. Christopher, K.R. Squire, World Pat. WO0018808, 2000.
- [38] Z. Hou, T.-a. Koizumi, M. Nishiura, Y. Wakatsuki, *Organometallics* 20 (2001) 3323.
- [39] O. Tardif, Z. Hou, T.-A. Koizumi, M. Nishiura, Y. Wakatsuki, *Organometallics* 20 (2001) 4565.
- [40] C.J. Schaverien, *Organometallics* 13 (1994) 69.
- [41] K. Tanaka, M. Furo, E. Ihara, H. Yasuda, *J. Polym. Sci.: Part A: Polym. Chem.* 39 (2001) 1382.
- [42] Z. Hou, Y. Zhang, H. Tezuka, P. Xie, O. Tardif, T.-A. Koizumi, H. Yamazaki, Y. Wakatsuki, *J. Am. Chem. Soc.* 122 (2000) 10533.
- [43] Z. Hou, Y. Zhang, M. Nishiura, Y. Wakatsuki, *Organometallics* 22 (2003) 129.
- [44] D.P. Long, P.A. Bianconi, *J. Am. Chem. Soc.* 118 (1996) 12453.
- [45] J. Gromada, T. Chenal, A. Mortreux, J.W. Ziller, F. Leising, J.-F. Carpentier, *Chem. Commun.* (2000) 2183.
- [46] J. Gromada, T. Chenal, A. Mortreux, J.W. Ziller, F. Leising, J.-F. Carpentier, *J. Mol. Catal. A: Chem.* 182–183 (2002) 525.
- [47] S. Bambirra, D.v. Leusen, A. Meetsma, B. Hessen, J.H. Teuben, *Chem. Commun.* (2001) 637.
- [48] Y. Chen, Y. Zhang, Z. Shen, R. Kou, L. Chen, *Eur. Polym. J.* 37 (2001) 1181.
- [49] P.G. Hayes, W.E. Piers, R. Macdonald, *J. Am. Chem. Soc.* 124 (2002) 2132.
- [50] S. Hajela, W.P. Schaefer, J.E. Bercaw, *J. Organomet. Chem.* 532 (1997) 45.
- [51] S.C. Lawrence, B.D. Ward, S.R. Dubberley, C.M. Kozak, P. Mountford, *Chem. Commun.* (2003) 2880.
- [52] C.G.J. Tazelaar, S. Bambirra, D.v. Leusen, A. Meetsma, B. Hessen, J.H. Teuben, *Organometallics* 23 (2004) 936.
- [53] R. Duchateau, C.T.v. Wee, A. Meetsma, J.H. Teuben, *J. Am. Chem. Soc.* 115 (1993) 4931.
- [54] K.B. Aubrecht, K. Chang, M.A. Hillmyer, W.B. Tolman, *J. Polym. Sci.: Part A: Polym. Chem.* 39 (2001) 284.
- [55] G.R. Giesbrecht, G.D. Whitener, J. Arnold, *J. Chem. Soc., Dalton Trans.* (2001) 923.
- [56] S. Bambirra, M.J.R. Brandsma, E.A.C. Brussee, A. Meetsma, B. Hessen, J.H. Teuben, *Organometallics* 19 (2000) 3197.
- [57] S. Bambirra, D.v. Leusen, A. Meetsma, B. Hessen, J.H. Teuben, *Chem. Commun.* (2003) 522.
- [58] S. Arndt, T.P. Spaniol, J. Okuda, *Angew. Chem. Int. Ed.* 42 (2003) 5075.