ELSEVIER

Coordination Chemistry Reviews 231 (2002) 1–22

COORDINATION
CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Recent developments in organolanthanide polymerization catalysts

Zhaomin Hou*, Yasuo Wakatsuki

Organometallic Chemistry Laboratory, RIKEN (The Institute of Physical and Chemical Research), Hirosawa 2-1, Wako, Saitama 351-0198, Japan

Received 7 December 2001; received in revised form 27 February 2002

Contents

Abstract . . . 1
1. Introduction . . . 1
2. Metallocene complexes . . . 2
    2.1 Synthesis . . . 2
    2.2 Polymerization of ethylene . . . 3
    2.3 Polymerization of styrene and 1-alkenes . . . 6
    2.4 Polymerization of dienes . . . 6
    2.5 Polymerization of (meth)acrylates, lactones, and other polar monomers . . . 7
    2.6 Copolymerization reactions . . . 8
        2.6.1 Copolymerization of nonpolar monomers . . . 8
        2.6.2 Copolymerization of nonpolar monomers with polar monomers . . . 9
        2.6.3 Copolymerization of polar monomers . . . 9
3. Half-metallocene complexes . . . 10
    3.1 Synthesis . . . 10
        3.1.1 Complexes bearing mixed C_5Me_5–monodentate-anionic ligands . . . 10
        3.1.2 Complexes bearing linked cyclopentadienyl–amido or –phosphido ligands . . . 12
    3.2 Polymerization of ethylene . . . 13
    3.3 Polymerization of styrene . . . 14
    3.4 Polymerization of 1-alkenes, dienes, and other monomers . . . 14
    3.5 Block copolymerization of ethylene with styrene . . . 15
4. Cyclopentadienyl-free complexes . . . 16
    4.1 Synthesis . . . 16
    4.2 Polymerization . . . 17
5. Conclusion and perspective . . . 19
References . . . 20

Abstract

This review describes recent advances in the synthesis and polymerization chemistry of organolanthanide complexes (including those of scandium and yttrium), with emphasis being placed on the complexes that show novel activity and selectivity in polymerization reactions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lanthanide; Rare earth; Polymerization; Cyclopentadienyl; Metallocene; Catalysis

1. Introduction

Organolanthanide chemistry has witnessed a spectacular growth in the past two decades [1–5]. In this development, the design and application of organolanthanide complexes as catalysts for polymerization and organic synthesis have occupied an especially

---

* Corresponding author. Tel.: +81-48-467-9393; fax: +81-48-462-4665

E-mail address: houz@postman.riken.go.jp (Z. Hou).

PII: S0010-8545(02)00111-X

important place [5–10]. Changing the ligand environment of a complex to modify its properties has been an important strategy for the development of more efficient or selective catalysts. So far, organolanthanide chemistry has been dominated mainly by metallocene complexes that bear two substituted or unsubstituted cyclopentadienyl ligands. There has been recently an impetus toward the search for new ligand systems to extend the lanthanide chemistry beyond the traditional realm of metallocene complexes. Toward this end, various mono-and polydentate ligand systems have been examined as an alternative for, or in addition to, a cyclopentadienyl ligand [11–14].

This article is intended to provide an overview on recent progress in the synthesis and polymerization chemistry of organolanthanide complexes. We have not attempted to make a totally comprehensive survey, but rather address the trends in this area, with emphasis being placed on the complexes that show novel activity and selectivity in polymerization reactions. On the basis of the ancillary ligand types, the discussions are divided into three major sections, i.e. metallocene complexes, half-metallocene complexes, and cyclopentadienyl-free complexes. Each section consists of synthesis of the typical complexes and their use as catalysts for polymerization reactions. Special attention is devoted to samarium(II) complexes and lanthanide(III) alkyl and hydride complexes, since they are most often encountered in polymerization reactions. For simplicity, the definition of the lanthanides in this article applies to scandium, yttrium, and the elements from lanthanum through to lutetium. A metallocene is defined as a complex bearing two substituted or unsubstituted cyclopentadienyl, indenyl, or fluorenyl units as ancillary ligands, while a half-metallocene as a complex bearing one such an ancillary ligand. The catalyst activity figures available in the literature for ethylene polymerization have been converted into units of g polymer (mmol catalyst)$^{-1}$ h^{-1} atm^{-1}, and are rated according to the scale given by Gibson et al. (<1, very low; 1–10, low; 10–100, moderate; 100–1000, high; >1000, very high) [15].

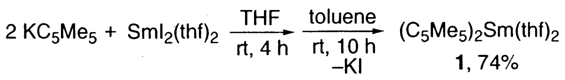
2. Metallocene complexes

2.1. Synthesis

Lanthanide metallocene complexes are the most extensively studied organolathanide compounds, on which many general and comprehensive reviews have already appeared [1–5]. This section is restricted mostly to the representative complexes that are active for polymerization reactions.

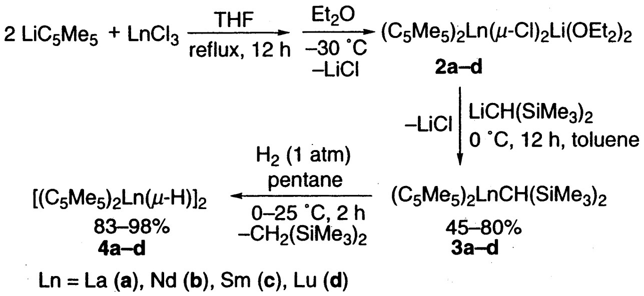
Lanthanide metallocene complexes with unsubstituted cyclopentadienyl ligands are almost insoluble in hydrocarbon solvents and usually show low activity [16–18]. However, pentamethylcyclopentadienyl ligand C_5Me_5 can generally provide excellent solubility and stability (isolability) for a metal ion, and is the most widely used ancillary ligand in organolanthanide chemistry. A general method for the synthesis of a lanthanide metallocene complex is the metathetical reaction between an alkali-metal salt of the ligand and the lanthanide halide. For example, the reaction of $SmI_2(thf)_2$ with 2 equiv. of KC_5Me_5 easily affords the samarocene(II) complex **1** (Scheme 1) [19]. Similar reactions of $LnCl_3$ with LiC_5Me_5 give the bis(pentamethylcyclopentadienyl)lanthanide(III) chloride complexes **2a**–**d**, which upon alkylation with $LiCH(SiMe_3)_2$ yield the corresponding metallocene alkyl complexes **3a**–**d** (Scheme 2) [20]. Hydrogenolysis of **3a**–**d** [20] or their allyl analogues [21] with H_2 easily produces the metallocene hydride complexes **4a**–**d**. In some cases, σ-bond metathesis of a metal–alkyl bond with a Si–H bond of $PhSiH_3$ also provides a convenient route to a lanthanide hydride complex [22].

Lanthanide metallocene complexes with various linked cyclopentadienyl ligands have also been prepared in a similar way. The synthetic routes to complexes bearing the silylene-linked, chelating bis(tetramethylcyclopentadienyl) ligands are shown in Scheme 3 [23]. Such linked cyclopentadienyl ligand systems can provide a more open coordination sphere for the metal center than the corresponding unlinked bis(cyclopentadienyl) ligand systems. Complexes with the linked, less bulky cyclopentadienyl ligand systems such as $[R_2Si(C_5Me_4)(C_5H_4)]^{2-}$ (R = Me or Et) [24], $[Me_2Si(C_5H_4)_2]^{2-}$ [25], and $[Me_2Si(C_5H_3R\text{-}3)_2]^{2-}$ (R = ^{t}Bu [26–28] or $SiMe_3$ (**10**) [29]), as well as those with the linked cyclopentadienyl–fluorenyl ligands (e.g. **11**–**13**) [30,31], have also been prepared analogously. In some of these complexes, particularly in the hydride complexes such as **8**–**10**, the ligands span two metal centers rather than chelate one [24,25,29].



$$2\,KC_5Me_5 + SmI_2(thf)_2 \xrightarrow[\text{rt, 4 h}]{\text{THF}} \xrightarrow[\text{rt, 10 h}\atop -\text{KI}]{\text{toluene}} \underset{\mathbf{1},\ 74\%}{(C_5Me_5)_2Sm(thf)_2}$$

Scheme 1.



Scheme 2.

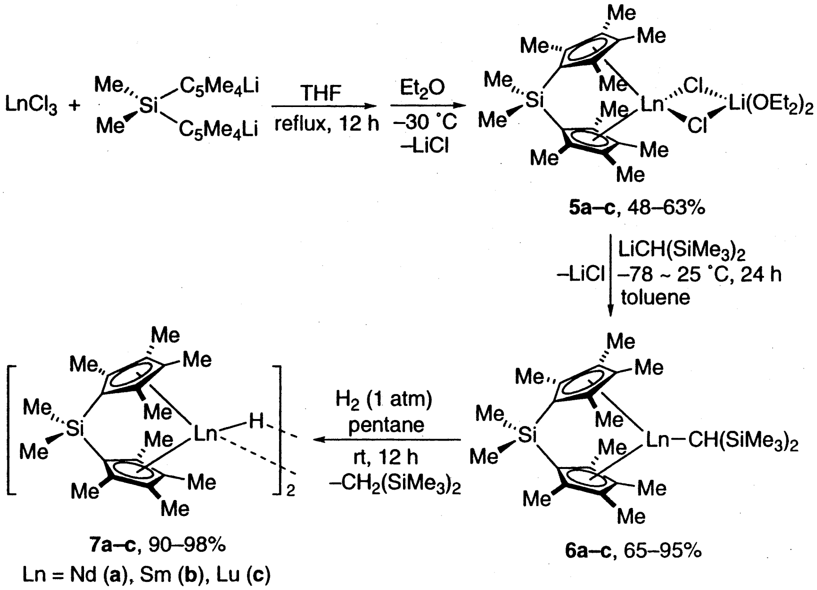
When each of the chelating bis(cyclopentadienyl) rings are partly substituted, two possible isomers (*racemic* and *meso*) can be formed, which in many cases can be separated from each other through crystallization. In some cases, *racemic–meso* isomerization can take place in solution through dissociation of one cyclopentadienide ligand from the metal, rotation around the Si–Cp$^-$ bond, and recoordination on the opposite face [27]. For [Me$_2$Si(C$_5$H$_2$(SiMe$_3$)-2-R-4)$_2$]$^{2-}$ (R = ^{t}Bu [32] or SiMe$_2^t$Bu [33]) which possess bulky trimethylsilyl substituents at the positions α to the dimethylsilylene linker, the metalation with yttrium affords almost exclusively the *racemic* isomers of the metallocene complexes (e.g. **14** and **15**), owing to steric repulsion between the SiMe$_3$ substituents in the narrow portion of the *meso*-metallocene wedge. Divalent samarium complexes bearing various linked cyclopentadienyl ligands, such as **16**–**19**, have also been prepared by the metathetical reactions of SmI$_2$ with the potassium salts of the corresponding ligands [34].

When the two methyl groups on the silylene linker in [Me$_2$Si(C$_5$H$_2$(SiMe$_3$)-2-^{t}Bu-4)$_2$]$^{2-}$ are replaced by the C_2-symmetric 1,1′-binaphth-2,2′-diolate group, enantioselective metalation of this ligand has been achieved, as a result of steric interactions between the 3-and 3′-methine positions of the 1,1′-binaphth-2,2′-diolate rings of the chiral linker and the α-trimethylsilyl substituents on the cyclopentadienyl rings [35]. Coordination of this ligand to yttrium occurs in an entirely diastereoselective manner: the ligand prepared from the (*R*)-(+)-1,1′-bi-2-naphtholate group directs formation of the (*S*)-yttrocenes (e.g. *R*,*S*-**20**), while that from the (*S*)-(−)-1,1′-bi-2-naphtholate group directs formation of the (*R*)-yttrocene complexes. Introduction of a chiral auxiliary (R*) such as (+)-neomenthyl, (−)-menthyl, or (−)-phenylmenthyl into the unsubstituted cyclopentadienyl ring of [Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_4$)]$^{2-}$ also enables the isolation of optically pure lanthanide metallocene complexes (e.g. **21** and **22**) [36]. Hydrogenolysis of the alkyl complexes such as **21** under 1 atm of H$_2$ at 25 °C in C$_6$D$_6$ proceeds rapidly to give CH$_2$(SiMe$_3$)$_2$ and an organometallic hydrido complex, as indicated by ^{1}H-NMR. However, unlike the achiral hydrido complexes such as **4a**–**c** and **7a**–**c**, the chiral hydrido species formed in this case are thermally unstable in solution at ambient temperature, and have not been isolated [36].

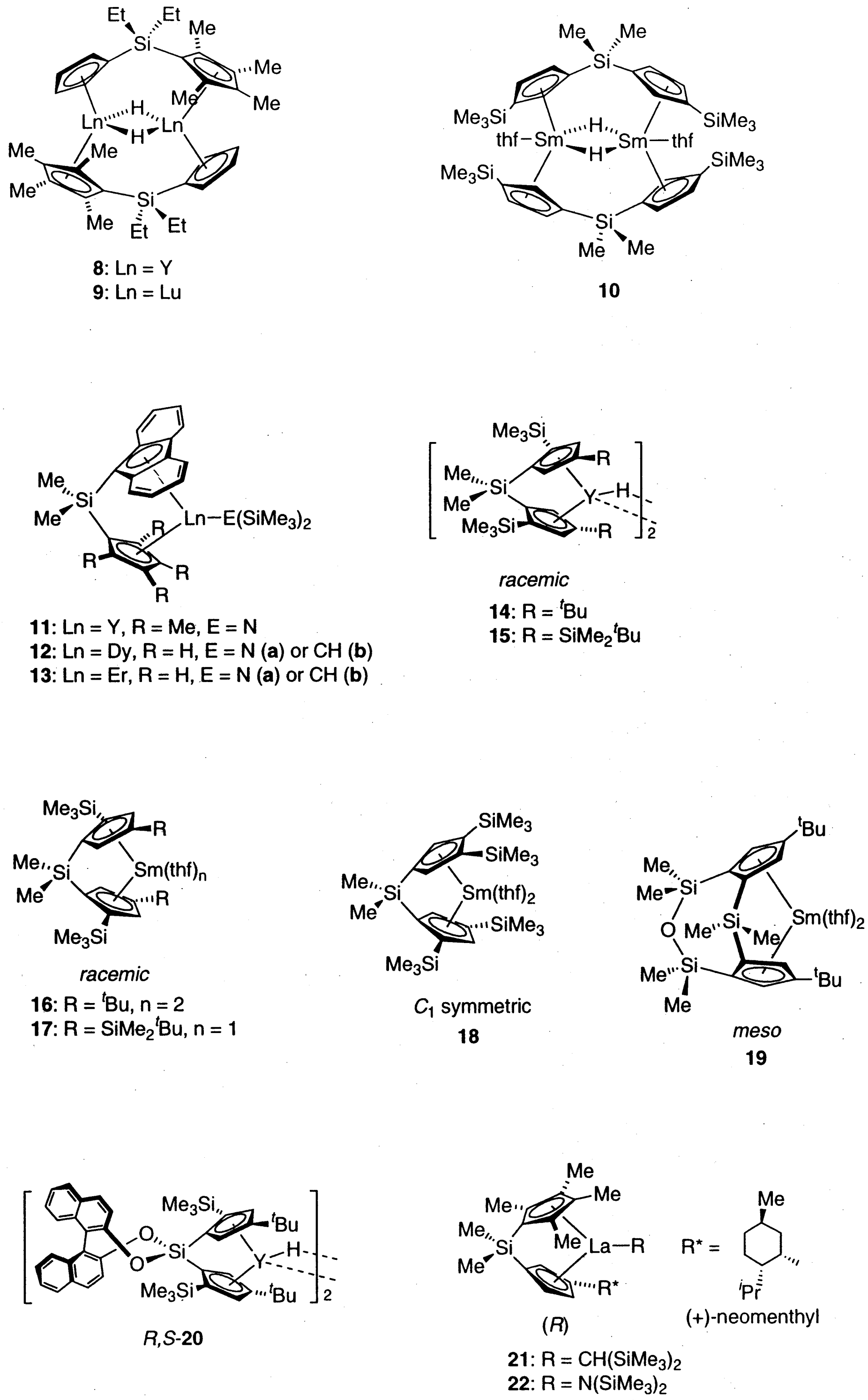
For the lanthanides that have an easily available +2 oxidation state, such as samarium, europium, and ytterbium, oxidation of their divalent metallocene complexes with appropriate substrates is also a convenient route to the corresponding lanthanidocene(III) complexes. For example, the reaction of 1,3-butadiene with **1** easily produces the corresponding samarocene(III) allyl complex **23** (Scheme 4), as a result of one-electron transfer from the Sm(II) to 1,3-butadiene followed by dimerization of the resultant radical anion species [37]. Oxidation of (C$_5^i$Pr$_4$H)$_2$Sm with 0.5 molar equiv. of *tert*-butylperoxide ^{t}BuOO^{t}Bu affords the alkoxide complex (C$_5^i$Pr$_4$H)$_2$SmO^{t}Bu [38]. The reaction of **1** with an excess of AlMe$_3$ yields the Sm(III)–Al(III) tetranuclear complex **24**, which exists in an equilibrium with the binuclear complex **25** in solution (Scheme 5) [39]. The similar reaction of (C$_5$Me$_5$)$_2$Yb(thf)$_2$ with AlEt$_3$ gives an adduct product, (C$_5$Me$_5$)$_2$Yb(μ,η^2-Et)AlEt$_2$(thf) [40].

2.2. Polymerization of ethylene

Lanthanide(III) metallocene alkyl and hydride complexes can serve as single component homogeneous catalysts for the polymerization of ethylene. Generally,



Scheme 3.



8: Ln = Y
9: Ln = Lu

10

11: Ln = Y, R = Me, E = N
12: Ln = Dy, R = H, E = N (**a**) or CH (**b**)
13: Ln = Er, R = H, E = N (**a**) or CH (**b**)

racemic
14: R = ^{t}Bu
15: R = SiMe$_2$^{t}Bu

racemic
16: R = ^{t}Bu, n = 2
17: R = SiMe$_2$^{t}Bu, n = 1

C_1 symmetric
18

meso
19

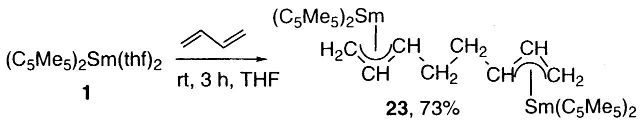
R,S-**20**

(*R*)
21: R = CH(SiMe$_3$)$_2$
22: R = N(SiMe$_3$)$_2$

R* = (+)-neomenthyl

Scheme 3 (*Continued*)

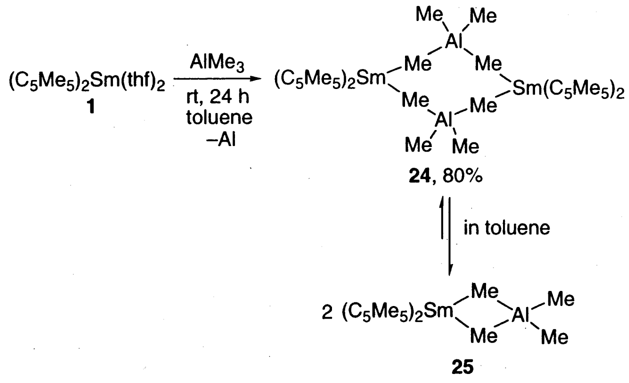
a hydride complex is much more active than its alkyl analogues. The first report on the application of organolanthanide complexes in ethylene polymerization appeared in 1978. Ballard et al. reported moderate catalytic activity at 70–100 °C (5–82 g mmol^{-1} h^{-1} atm^{-1}, $M_n = 1.5 \times 10^3$–1.4×10^4, $M_w/M_n = 1.5$–2.7) using metallocene alkyl complexes [(C$_5$H$_4$R′)$_2$LnR]$_2$ (Ln = Y, Er; R = Me, ^{n}Bu, AlMe$_4$; R′ = H, Me, Et, SiMe$_3$) [41]. A few years later, Watson et al. described ethylene polymerization by the lutetium methyl complex [(C$_5$Me$_5$)$_2$LuMe]$_2$ at 50–80 °C (ca. 70 g mmol^{-1} h^{-1} atm^{-1}) [6]. Marks and co-workers have made a more



Scheme 4.

detailed investigation on ethylene polymerization using a series of lanthanide metallocene alkyl and hydride complexes. They find that the metallocene hydride complexes $[(C_5Me_5)_2LnH]_2$ (**4**: Ln = La, Nd, Lu) are very active catalysts to yield high molecular weight polyethylene (initial activity (< 10 s) up to 146400 g $mmol^{-1}$ h^{-1} atm^{-1}, M_n up to 6.76×10^5, $M_w/M_n = 1.37–6.42$) [20]. The polymerization activity generally increases with the ion radius of the metal ($La \geq Nd \gg Lu$). The bis(trimethylsilyl)methyl metallocene complexes $(C_5Me_5)_2LnCH(SiMe_3)_2$ (**3**: Ln = La, Nd, Sm, Lu) are inactive for ethylene polymerization under the same conditions. Bercaw and co-workers have used a series of scandium metallocene complexes $(C_5Me_5)_2ScR$ (R = H or alkyl) as a model for the mechanistic study of Ziegler–Natta polymerization of ethylene [42]. They found that the order of the ethylene insertion rate is $Sc–H \gg Sc–CH_2CH_2CH_3 \geq Sc–CH_2(CH_2)_nCH_3$ $(n \geq 2) > Sc–CH_3 > Sc–CH_2CH_3 > Sc–C_6H_5$. Evans and coworkers have recently found that the extremely sterically crowded tris(pentamethylcyclopentadienyl)samarium complex $(C_5Me_5)_3Sm$ can initiate the polymerization of ethylene, possibly via an η^1-C_5Me_5 intermediate such as $(\eta^5\text{-}C_5Me_5)_2Sm(\eta^1\text{-}C_5Me_5)$ [43]. The Sm–Al heterometallic complex **24** has also been found to be active for ethylene polymerization [39].

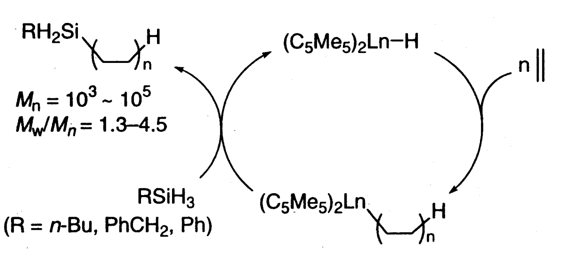
Metallocene hydride complexes with the silylene-linked tetramethylcyclopentadienyl ligands such as **7a**–**c** provide a more open ligand sphere for the metal center than the unlinked analogues, and can show higher activity. For a given lanthanide, complexes of the type $Me_2Si(C_5Me_4)_2LnH$ are reported to be ca. ten times more active than those of the type $(C_5Me_5)_2LnH$ [23]. In contrast to the $(C_5Me_5)_2$-and $Me_2Si(C_5Me_4)_2$-ligated hydride complexes such as **4a**–**d** and **7a**–**c**, the $Me_2Si(C_5Me_4)(C_5H_5)$-based hydride complexes such as **8** and **9** do not polymerize ethylene, probably because of the 'spanning' ligation structure in the latter case [24]. The 'spanover' dimer **10**, however, exhibits a moderate activity for ethylene polymerization (27 g $mmol^{-1}$ h^{-1} atm^{-1}, $M_n = (3–5) \times 10^4$, $M_w/M_n = 1.63–1.68$) [29]. The *racemic* yttrocene hydride complexes **14** and **15**, which are originally designed for polymerization of α-olefins, show high activity also for ethylene polymerization (**15**: ~500 g $mmol^{-1}$ h^{-1} atm^{-1}, $M_n = \sim 10^5$, $M_w/M_n = \sim 4$) [32,33], while the activity of similar lanthanidocene alkyl complexes has been found much lower [44,45].



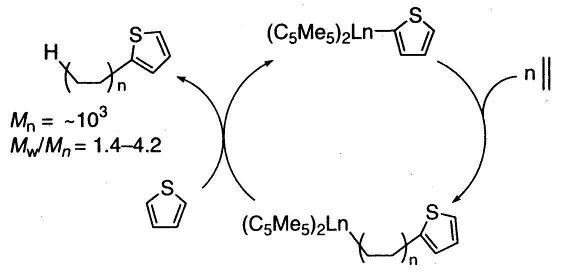
Scheme 5.

Primary silanes such as $PhSiH_3$, $PhCH_2SiH_3$, and n-$BuSiH_3$ can be used as chain transfer agents in the organolanthanide-catalyzed polymerization of ethylene to give the silyl-capped polyethylenes [46]. A possible catalytic cycle is shown in Scheme 6. The use of thiophene in place of a silane affords the thienyl-capped polyethylene (Scheme 7) [47]. In this case, the 2-thienyl complex $(C_5Me_5)_2La(2\text{-}C_4H_3S)$, which can be easily produced by the reaction of $(C_5Me_5)_2LaH$ with thiophene, acts as a true catalyst species.

Divalent samarium metallocene complexes can also effect ethylene polymerization, initially through one-electron transfer from the Sm(II) center to an ethylene monomer to form a Sm(III)–carbon bond that is active for ethylene insertion [34,48]. The less reducing Yb(II) and Eu(II) metallocene complexes are generally inactive for ethylene polymerization. As in the case of lanthanide(III) metallocene complexes, the polymerization behavior of a Sm(II) metallocene complex is strongly influenced by the ancillary ligands. The bis(pentamethylcyclopentadienyl)samarium(II) complexes $(C_5Me_5)_2Sm(thf)_x$ $(x = 0–2)$ usually produce polyethylenes with relatively low molecular weights ($M_n < 2.5 \times 10^4$) [34,49]. Among a series of linked bis(cyclopentadienyl)samarium(II) complexes such as **16**–**19**, which are developed by Yasuda and co-workers, the *meso* type complex **19** shows the highest activity for ethylene polymerization (470 g $mmol^{-1}$ h^{-1} atm^{-1}, $M_n = 4.7 \times 10^4$, $M_w/M_n = 3.49$), while the C_1-symmetric complex **18** affords the highest molecular weight of polyethylene (14 g $mmol^{-1}$ h^{-1} atm^{-1}, $M_n = 1.45 \times 10^6$, $M_w/M_n = 1.60$) [34]. The *racemic* complex **16** is in



Scheme 6.



Scheme 7.

between, which shows a moderately high activity and yields moderately high molecular weight polymer (139 g $mmol^{-1}$ h^{-1} atm^{-1}, $M_n = 3.56 \times 10^5$, $M_w/M_n = 1.60$).

2.3. Polymerization of styrene and 1-alkenes

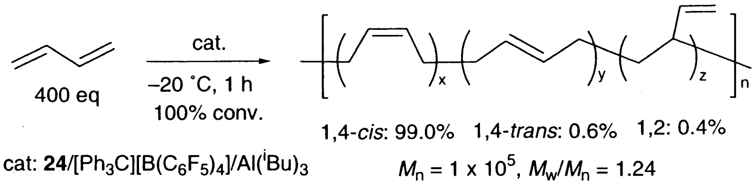
The polymerization of styrene by a lanthanide metallocene complex is much more difficult than that of ethylene owing to steric hindrance. The reaction of $(C_5Me_5)_2Sm$ with an excess of styrene in toluene yields a stable bimetallic complex, $[(C_5Me_5)_2Sm]_2(\mu\text{-}CH_2CHPh)$ [50], which is inert toward styrene even under very high pressure (> 5000 atm) [48,51]. Complexes bearing the less sterically demanding $C_5H_4^tBu$ ligand, such as $[(C_5H_4^tBu)_2LnMe]_2$ (Ln = Pr, Nd, Gd) [52], $[(C_5H_4^tBu)_2Yb(thf)_2][BPh_4]$ [53], and $(C_5H_4^tBu)_2YbAlH_3(OEt_2)$ [54] are reported to show an activity for styrene polymerization at high temperatures (50–100 °C, 66–96% yield, 0.1–1 mol% Ln, 5–60 h), affording atactic polystyrenes. The bulk polymerization of styrene at 105 °C with the combination of a chlorolanthanidocene complex such as $(C_5Me_5)_2NdCl_2Li(OEt_2)_2$ and a dialkylmagnesium compound has also been reported [55]. The role played by the lanthanide species in these polymerizations is, however, yet to be further clarified.

Achiral lanthanidocene complexes such as **1**, **4a**–**d**, and **7a**–**c** are generally inactive for 1-alkene polymerization, owing to formation of stable η^3-allyl type complexes [20,23,37]. Alkene complexation and alkyl migration in some bis(pentamethylcyclopentadienyl)-yttrium–alkyl–alkene complexes have been observed at low temperatures (< −100 °C) by NMR spectroscopy [56–58]. In contrast, a series of lanthanide *rac*-metallocene complexes have been reported to act as single component catalysts for the polymerization of 1-alkenes. The *rac*-yttrocene hydride **14**, developed by Bercaw and coworkers, constitutes the first iso-specific organolanthanide 1-alkene polymerization catalyst [32]. Propylene as well as neat 1-butene, 1-pentene, and 1-hexene are all polymerized, albeit rather slowly over a period of several days at 25 °C to afford modest molecular weight polymers (polypropylene: $M_n = 4.2 \times 10^3$, $M_w/M_n = 2.32$, 97.0% *mmmm*; poly(1-butene): $M_n = 8.5 \times 10^3$, $M_w/M_n = 3.44$; poly(1-pentene): $M_n = 2.0 \times 10^4$, $M_w/M_n = 1.99$; poly(1-hexene): $M_n = 2.4 \times 10^4$, $M_w/M_n = 1.75$). By replacement of the *tert*-butyl groups in the ligand array of **14** with the more sterically demanding $SiMe_2(^tBu)$ groups, Yasuda and co-workers have prepared a more active catalyst (**15**), which polymerizes 1-pentene and 1-hexene at 0 °C or room temperature to afford in high yields (77–99%) polymers with $M_n = (1–5) \times 10^4$, $M_w/M_n = 1.50–2.46$, and high degrees of isotacticity (*mmmm* > 95%) [33]. The enatiomerically pure yttrocene hydride (*R*,*S*)-**20** also shows high activity for the iso-specific polymerization of 1-pentene ($M_n = 1.19 \times 10^5$, $M_w/M_n = 1.44$, *mmmm* > 95%). Among the linked bis(cyclopentadienyl)samarium(II) complexes **16**–**19**, only the *racemic* complexes **16** and **17** showed activity, albeit low, for the polymerization of 1-pentene and 1-hexene (~ 0.1 g $mmol^{-1}$ h^{-1}, M_n = ~ 1×10^4, $M_w/M_n = 1.48–1.70$, *mmmm* > 95%) [34].

The lutetium metallocene hydride $[(C_5Me_5)_2LuH]_2$ is an active catalyst for the ring-opening polymerization of methylenecyclopropane to yield the *exo*-methylene-functionalized polyethylene $[CH_2CH_2C(CH_2)]_n$ [59]. In contrast, $[(C_5Me_5)_2LaH]_2$ and $[(C_5Me_5)_2SmH]_2$ effect the catalytic 'ring-expanding' dimerization of methylenecyclopropane to give the dimer 1,2-dimethylene-3-methylcyclopentane [59].

2.4. Polymerization of dienes

As a single component, lanthanide metallocene complexes are generally inactive for the polymerization of butadiene, owing to easy formation of stable η^3-allyl type complexes (cf. Scheme 4) [20,23,37]. Upon addition of a co-catalyst, however, such complexes can serve as an excellent catalytic system for butadiene polymerization. Work in our group has shown that when treated with MMAO (modified methylaluminoxane containing isobutylaluminoxane) or $Al(^iBu)_3$–$[Ph_3C][B(C_6F_5)_4]$, lanthanide metallocene complexes such as **1** and **24** rapidly initiate the 1,4-*cis*-stereospecific polymerization of 1,3-butadiene in a living fashion to yield polybutadienes with extremely high contents of the 1,4-*cis* microstructure (up to 99.5%), high molecular weights (M_n up to 10^6), and narrow molecular weight distributions ($M_w/M_n = 1.2–1.8$) (Scheme 8) [60–62]. Although the polymerization of 1,3-butadiene has been extensively studied with various catalytic systems, this is the first example ever reported to afford a polymer with both high content of the 1,4-*cis*-polybutadiene microstructure (> 98%) and narrow molecular weight distribution ($M_w/M_n < 2$). Such polymers are expected to be of various practical uses as highly elastic and wearable synthetic rubber materials. The catalyst species in this system is thought to be an alkyl-bridged Sm(III)–Al(III) heterometallic cation, although details are yet to be clarified. Anionic samarocene(III) bis(allyl) complexes such as $[(Me_2C)_2(C_5H_4)_2Sm(C_3H_5)_2]Li(dme)$ (dme = dimethox-



Scheme 8.

yethane) are reported to initiate 1,4-*trans*-polymerization of isoprene through dissociation of LiC_3H_5 [63].

1,5-hexadiene can be cyclopolymerized by the *rac*-yttrocene hydride complex **15**, yielding poly(methylene-1,3-cyclopentanediyl) as a 45/55 *cis–trans* mixture ($M_n = 1.37 \times 10^5$, $M_w/M_n = 2.44$) [33]. This cyclopolymerization can also be effected by the *rac*-samarocene(II) complex **16**, albeit much more slowly [34]. In contrast, the scandocene(III) hydride complexes $Me_2Si(C_5Me_4)_2ScH(PMe_3)$ and $[Me_2Si(C_5H_3{}^tBu\text{-}3)_2ScH]_2$ catalytically cyclize a range of α,ω-dienes to methylenecycloalkanes rather than cyclopolymerize them [64].

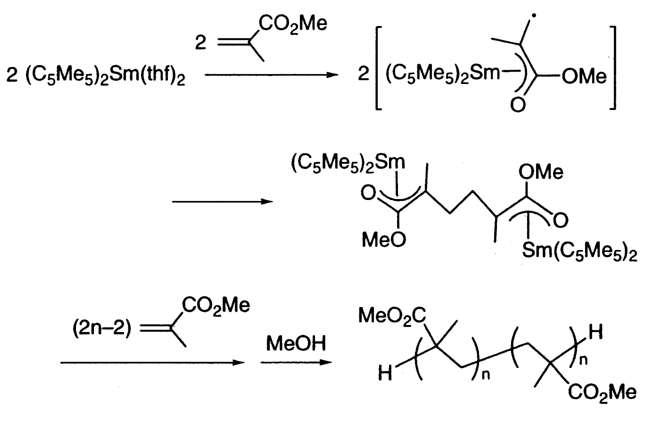
2.5. Polymerization of (meth)acrylates, lactones, and other polar monomers

Yasuda and co-workers have found that bis(pentamethylcyclopentadienyl)lanthanide hydride or methyl complexes such as $[(C_5Me_5)_2LnR]_2$ (Ln = Y, Sm, Lu; R = H, Me) act as excellent initiators for the living polymerization of (meth)acrylates.[65–67] In the case of methyl methacrylate (MMA), highly syndiotactic polymers (up to 95% *rr*) with high molecular weights ($M_n = \sim 10^5$) and extremely narrow polydispersities ($M_w/M_n = 1.02–1.05$) have been obtained [65,66]. The polymerization is initiated by 1,4-addition of the methyl or hydride to one molecule of MMA, followed by 1,4-addition of the resultant enolate to another molecule of MMA. An eight-membered-ring enolate intermediate, which is active for syndio-specific living polymerization of MMA, has been isolated from the reaction of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ with 2 equiv. of MMA (per Sm).

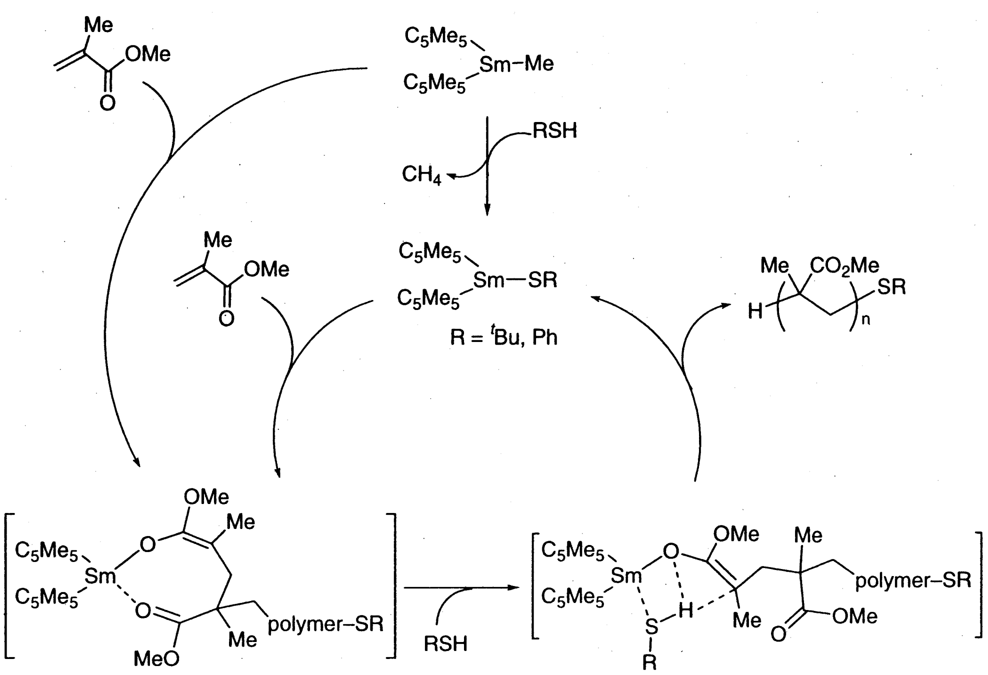
The stereoselectivity in the organolanthanide-mediated MMA polymerizations appears to be very susceptible to variation in the ligand array of the initiators. Marks and co-workers have investigated the stereocontrol in MMA polymerization using various chiral lanthanide metallocene complexes, and accomplished high isotactic selectivity (94% mm) when the chiral lanthanocene amido complex **22** is used as an initiator [68]. Do and co-workers obtained iso-rich poly(MMA) by using the silylene-linked fluorenyl–tetramethylcyclopentadienyl yttrium amido complex **11** as an initiator [30], while Qian and co-workers observed syndio-rich polymer formation in the case of the less bulky, analogous complexes such as **12** and **13** [31]. *rac*-1,1′-(3-Oxapentamethylene)-bridged bis(indenyl) lanthanidocenes [69] and bis(methylcyclopentadienyl)lanthanide amido complexes [70,71] have also been investigated; they showed less stereoselectivity in MMA polymerization.

Bimetallic complexes such as **23** and $[(C_5Me_5)_2Sm]_2(\mu\text{-}N_2Ph_2)$ can act as bifunctional initiators for the syndiospecific living polymerization of MMA, as shown by Boffa and Novak [72,73]. Samarocene(II) complexes such as $(C_5Me_2)_2Sm(thf)_2$ are more efficient bisinitiators for MMA polymerization, since one-electron transfer from the Sm(II) to the monomer easily generates a radical anion species which subsequently couples into a bimetallic samarium(III) enolate that acts as a bisinitiator for the polymerization (Scheme 9) [74]. The polymerization of MMA by the bis(trimethylsilylindenyl or fluorenyl)-ligated ytterbium(II) complexes has also been reported; this yields iso-rich polymers at low temperature [75,76].

Chain transfer polymerization of MMA can be achieved by the use of appropriate acidic organic compounds such as thiols or methyl ketones as chain transfer agents. Nodono and co-workers have successfully synthesized a series of thienyl-and ketone-capped poly(MMA)s ($M_n = (1–7) \times 10^4$, $M_w/M_n = 1.4–2.1$) by addition of $(C_5Me_2)_2SmMe(thf)$ to a mixture of MMA and a chain transfer agent such as ^{t}BuSH, PhSH, MeCO^{i}Bu, or MeCOPh [77]. The molecular weights and molecular-weight distributions of the resulting polymers vary with the amount of the chain transfer agents used. Thiols are more effective than ketones as chain transfer agents, since lanthanide thiolate is able to initiate the living polymerization of MMA [78], while



Scheme 9.



Scheme 10.

lanthanide alkoxide, which in this case could be formed by nucleophilic addition of the Sm–Me to the C–O double bond of a ketone, is inactive toward MMA. A possible catalytic cycle for the chain transfer polymerization of MMA in the presence of a thiol is shown in Scheme 10 [77]. The chain-end-capped poly(MMA)s showed improved thermal degradability and optical properties.

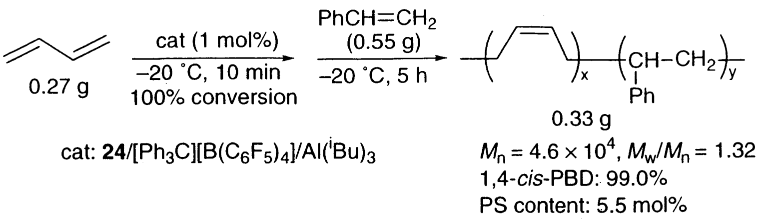
The ring-opening polymerization of lactones such as ε-caprolactone and δ-valerolactone can be effected in a living fashion by bis(pentamethylcyclopentadienyl)lanthanide hydride, alkyl, or alkoxide complexes, which afford linear polyesters with high molecular weights (M_n up to 1.4×10^5) and extremely narrow polydispersities ($M_w/M_n = 1.05–1.12$) [79]. The initiation step involves nucleophilic attack of the hydride, alkyl or alkoxide group on the carbonyl carbon atom of a lactone. Samarocene(II) complexes, such as $(C_5Me_2)_2Sm(thf)_2$, can also initiate the ring-opening polymerization of ε-caprolactone, but yield polymers with broader or bimodal molecular weight distributions ($M_w/M_n = 1.4–2.5$).[80,81] The ring-opening polymerization of ε-caprolactone by the Y–Li heterobimetallic metallocene complexes such as $Li[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2X)_2]$ (X = OMe, NMe_2) affords cyclic polyesters with moderate polydispersities ($M_w/M_n < 2$) [82]. As in the case of MMA, bimetallic Sm(III) complexes such as **23** can serve as bifunctional initiators for the ring-opening polymerization of lactones [72].

Yttrium and lanthanum metallocene hydrides $[(C_5Me_5)_2LnH]_2$ are active catalysts for the oligomerization of 2-cyclopenten-1-one ($P_n \leq 15$) [83]. $(C_5Me_5)_2LnCH(SiMe_3)_2$ (Ln = La, Nd) can effect catalytic dimerization of aldehydes to esters. This reaction is applicable to the synthesis of polyesters from dialdehydes [84]. The reactions of 1 equiv. of phenyl isocyanate with the lanthanidocene amido complexes $(C_5H_4Me)_2LnN(^iPr)_2(thf)$ (Ln = Y, Er, Yb) yield the structurally characterizable insertion products $(C_5H_4Me)_2Ln[\eta\text{-}OC(N^iPr_2)NPh](thf)$ [85]. Such complexes are reported to be active for the polymerization of phenyl isocyanate [85] and ε-caprolactone [86]. Catalytic dehydrogenative oligomerization of $PhSiH_3$ by samarocene(II) or lanthanidocene(III) hydride or alkyl complexes has also been reported [87].

2.6. Copolymerization reactions

2.6.1. Copolymerization of nonpolar monomers

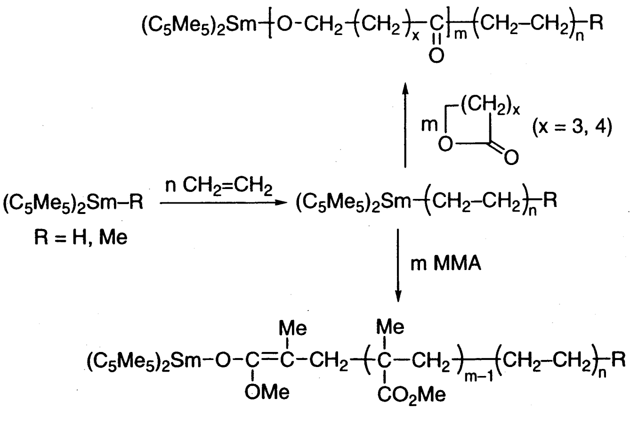
Marks and co-workers have shown that the lanthanide metallocene hydride complexes $[(C_5Me_5)_2LnH]_2$ (Ln = La, Sm, Lu) are able to copolymerize ethylene with methylenecyclopropane to afford the random copolymers $[(CH_2CH_2)_x(CH_2CH_2C(CH_2))_y]_n$ with M_n up to 4×10^4 and $M_w/M_n = 1.8–4.4$.[59] The activity in incorporating methylenecyclopropane into the polymer follows the order: Lu > Sm > La. In the presence of $PhSiH_3$ or n-$BuSiH_3$, the *ansa*-samarocene alkyl complex $Me_2Si(C_5Me_4)_2SmCH(SiMe_3)_2$ (**6b**) effects the copolymerization of ethylene with 1-hexene or styrene to give the corresponding silyl-capped random copolymers with $M_n = \sim 10^3$ and $M_w/M_n = 1.4–4.9$ [46]. In contrast, the *rac*-metallocene complexes **14**–**17**, which are active for the homopolymerization of both ethylene and



Scheme 11.

1-alkenes, do not copolymerize these two types of monomers, but yield only homopolyethylene under the presence of both monomers. Evans and coworkers have investigated the '$(C_5Me_5)_2Sm$'-catalyzed copolymerization of ethylene with styrene[48] or α-olefins [88] by use of field desorption mass spectrometry. They found that the incorporation of styrene or an α-olefin was no more than two molecules per polyethylene chain.

Work in our laboratory has shown that the living, 1,4-*cis*-stereospecific butadiene polymerization catalyst **24**–$Al(^iBu)_3$–$[Ph_3C][B(C_6F_5)_4]$ is active also for styrene polymerization, which upon sequential reaction with butadiene and styrene, affords block butadiene–styrene copolymers with extremely high contents of the 1,4-*cis*-polybutadiene microstructure (99%) (cf. Scheme 11) [60,62]. When the copolymerization reactions are carried out in the presence of both monomers, random butadiene–styrene copolymers (styrene content = 4.6–33.2 mol%) with high contents of the 1,4-*cis*-polybutadiene microstructure (80–95%), high molecular weights (M_n up to 1×10^5), and relatively narrow molecular weight distributions ($M_w/M_n = 1.4$–2.3) have been obtained. Visseaux and co-workers have reported that the anionic *ansa*-samarocene(III)–lithium bis(allyl) complex $[(Me_2C)_2(C_5H_4)_2Sm(C_3H_5)_2]Li(dme)$ is active for the copolymerization of isoprene with C_6–C_{18} 1-alkenes to give random copolymers with the 1,4-*trans*-polyisoprene microstructure and 6–10% of 1-alkene content [89].



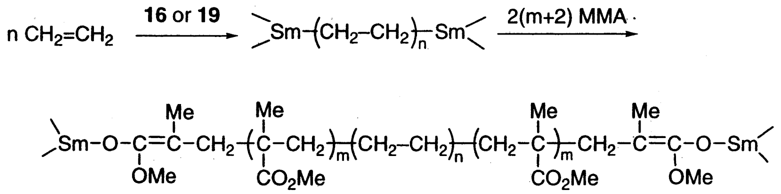
Scheme 12.

2.6.2. Copolymerization of nonpolar monomers with polar monomers

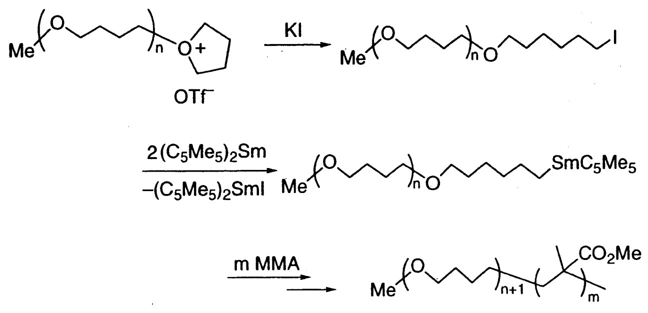
Since the insertion of an acrylate or lactone into the propagating metal alkyl to form an enolate or alkoxide is energetically favorable, block copolymers of ethylene or 1-alkenes with (meth)acrylates or lactones can be prepared by sequential monomer addition to the lanthanide catalysts. Yasuda and co-workers have shown that the AB diblock copolymers of ethylene with MMA, methyl acrylate, ethyl acrylate, ε-caprolactone, or δ-valerolactone can be easily synthesized by sequential introduction of ethylene and the polar monomer into a toluene solution of $[(C_5Me_5)_2SmH]_2$, $[(C_5Me_5)_2SmMe(thf)]_2$ or **10** (Scheme 12) [29,90]. The diblock copolymers of 1-pentene or 1-hexene with MMA or ε-caprolactone can be obtained by the use of the *rac*-yttrocene hydride **14** or **15** as an initiator [91]. Divalent samarocene complexes such as **16** and **19** act as a unique catalyst for the synthesis of the ABA triblock copolymers of ethylene with MMA, ε-caprolactone, or 2,2-dimethyltrimethylene carbonate, since ethylene can be reductively coupled by the Sm(II) to generate a bimetallic Sm(III) alkyl species that acts as a bisinitiator for the polymerization (Scheme 13) [92]. The reverse monomer addition, i.e. a polar monomer followed by a nonpolar monomer, does not give the copolymers because the conversion of an enolate (or alkoxide) to an alkyl is not favored.

2.6.3. Copolymerization of polar monomers

Analogously to the above bisinitiated nonpolar–polar copolymerizations, highly syndiotactic ABA triblock copolymers containing both methacrylate and acrylate segments have been prepared in two monomer-addition steps by the use of a samarocene(II) complex such as $(C_5Me_5)_2Sm(thf)_2$ as an initiator [74]. Sequential addition of MMA and a lactone such as ε-caprolactone, δ-valerolactone, or β-propiolactone to a toluene solution of $(C_5Me_5)_2SmMe(thf)$ affords the corresponding AB diblock MMA–lactone copolymers [79]. The random copolymerization of methyl acrylate with ethyl acrylate or *n*-butyl acrylate [67] and that of ε-caprolactone with δ-valerolactone or β-propiolactone [79] have been achieved by addition of a mixture of the monomers to an initiator such as $(C_5Me_5)_2SmMe(thf)$.



Scheme 13.



Scheme 14.

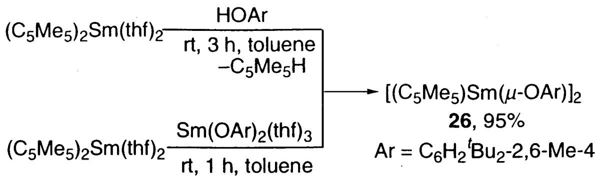
Endo and co-workers have used the samarocene(II) complex $(C_5Me_5)_2Sm$ to convert the cationic growing center of the living poly(tetrahydrofuran) [poly(THF)] into an anionic one by reduction of the in-situ prepared, iodide-end-capped poly(THF), as shown in Scheme 14 [93]. The resultant macroanion species effects the polymerization of a variety of electrophilic monomers such as δ-valerolactone, 2-oxo-1,3-dioxane, and alkyl methacrylates to give the corresponding poly(THF)–poly(electrophile) block copolymers.

3. Half-metallocene complexes

3.1. Synthesis

3.1.1. Complexes bearing mixed C_5Me_5–monodentate-anionic ligands

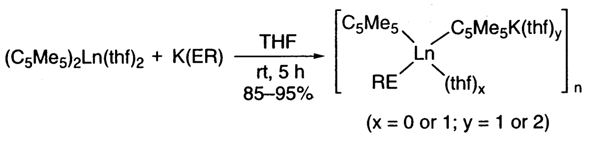
Generally, the isolation of a lanthanide half-metallocene complex bearing mixed cyclopentadienyl–monodentate-anionic ligands is more difficult than that of a metallocene, because of ligand redistribution problems. However, by the use of appropriate ligand combinations, several types of such half-metallocene complexes have been isolated and have had their reactivity studied.



Scheme 15.

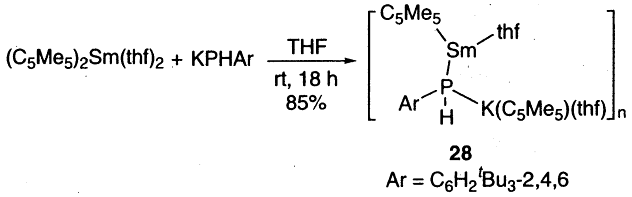
Partial protonation of $(C_5Me_5)_2Sm(thf)_2$ with 1 equiv. of HOAr (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4) or metathesis of $(C_5Me_5)_2Sm(thf)_2$ with 1 equiv. of $Sm(OAr)_2(thf)_3$ in toluene easily affords the C_5Me_5–OAr-ligated Sm(II) complex **26**, which adopts a dimeric structure via the μ-OAr bridges (Scheme 15) [94]. An attempt to synthesize **26** by the metathetical reaction between $Sm(OAr)_2(thf)_3$ and 1 equiv. of KC_5Me_5 affords $[(C_5Me_5)Sm(OAr)(C_5Me_5)K(thf)_2]_n$ (**27a**), which can formally be viewed as a '$(C_5Me_5)K(thf)_2$' adduct of the monomeric form of **26**. In fact, addition of 1 equiv. of KC_5Me_5 (per Sm) to a THF solution of **26** gives **27a** in 80–85% isolated yields. The most efficient route to **27a** is the reaction of $(C_5Me_5)_2Sm(thf)_2$ with 1 equiv. of KOAr. This method has been successfully extended to the synthesis of the analogous thiolate (**27c**) [95], amide (**27e–f**) [95], silyl (**27g–i**) [96], and alkyl (**27j–l**) [97] lanthanide(II) complexes as shown in Scheme 16. Complexes **27a–l** all can be viewed as a C_5Me_5–ER-ligated-Ln(II) species stabilized by the neutral 'C_5Me_5K' ligand. The 'intermolecular' interaction between the K atom and a C_5Me_5 ligand constitutes a similar polymeric structure in all of these complexes.

The analogous reaction of $(C_5Me_5)_2Sm(thf)_2$ with 1 equiv. of KPHAr (Ar = $C_6H_2{}^tBu_3$-2,4,6) yields the phosphide complex **28** (Scheme 17) [95]. In contrast with **27a–l**, in which the 'C_5Me_5K' unit is bonded to the Ln(II) center through the C_5Me_5 part, the 'C_5Me_5K' unit in **28** is bonded to the phosphide site with its K atom, probably owing to the stronger electron-donating

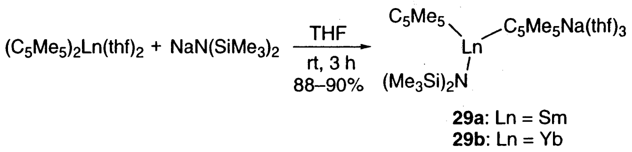


27a: Ln = Sm; ER = $OC_6H_2{}^tBu_2$-2,6-Me-4
27b: Ln = Sm; ER = $OC_6H_3{}^iPr_2$-2,6
27c: Ln = Sm; ER = $SC_6H_2{}^iPr_3$-2,4,6
27d: Ln = Sm; ER = $NHC_6H_2{}^tBu_3$-2,4,6
27e: Ln = Sm; ER = $N(SiMe_3)_2$
27f: Ln = Yb; ER = $N(SiMe_3)_2$
27g: Ln = Sm; ER = SiH_3
27h: Ln = Yb; ER = SiH_3
27i: Ln = Eu; ER = SiH_3
27j: Ln = Sm; ER = $CH(SiMe_3)_2$
27k: Ln = Yb; ER = $CH(SiMe_3)_2$
27l: Ln = Eu; ER = $CH(SiMe_3)_2$

Scheme 16.



Scheme 17.

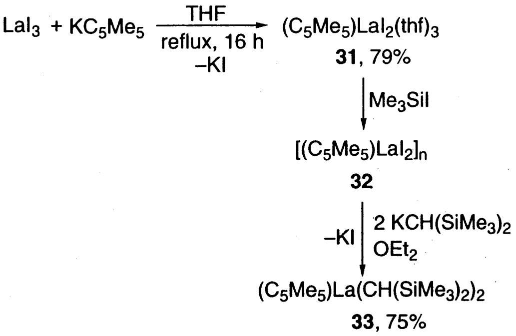


Scheme 18.

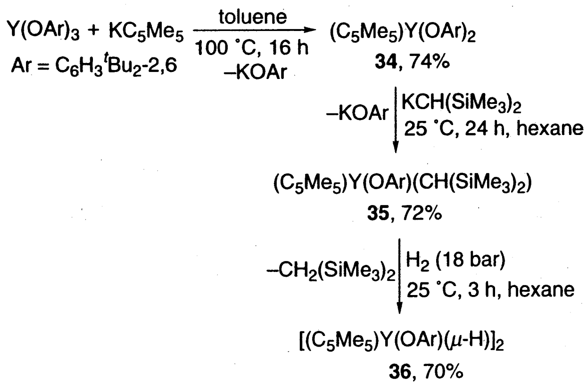
ability of the phosphide ligand. ‘C_5Me_5Na’ can also act as a stabilizing ligand for the C_5Me_5–$N(SiMe_3)_2$-ligated lanthanide(II) complexes. The use of $NaN(SiMe_3)_2$ in place of $KN(SiMe_3)_2$ in the reaction with $(C_5Me_5)_2Ln(thf)_2$ gives the ‘$C_5Me_5Na(thf)_3$’-coordinated Ln(II) complexes **29a**,**b** (Ln = Sm, Yb), which adopt a ‘monomeric’ structure owing to coordination of three thf ligands to the Na atom (Scheme 18) [95].

The ‘CpK’ ligation can also be applied to samarium(II) complexes bearing linked-bis(cyclopentadienyl) groups. The reaction of $Me_2Si(C_5Me_4)_2Sm(thf)_2$ with 1 equiv. of KOAr (Ar = $C_6H_2^tBu_2$-2,6-Me-4) in THF yields **30**, which can formally be viewed as a C_5Me_4–OAr-ligated Sm(II) species coordinated by the silylene-linked ‘C_5Me_4K’ unit (Scheme 19) [95].

The reaction of LaI_3 with 1 equiv. of KC_5Me_5 in THF affords the mono(pentamethylcyclopentadienyl)lanthanum diiodide complex **31** [98], which upon treatment with Me_3SiI yields the unsolvated analogue **32** (Scheme 20) [99]. The metathetical reaction of **32** with 2 equiv. of $KCH(SiMe_3)_2$ gives straightforwardly the dialkyl complex **33** [99]. Similarly, the reaction of $(C_5Me_5)Ce(OAr)_2$ (Ar = $C_6H_3^tBu_2$-2,6) with 2 equiv. of $LiCH(SiMe_3)_2$ affords the (pentamethylcyclopentadienyl)cerium dialkyl complex $(C_5Me_5)Ce(CH(SiMe_3)_2)_2$ [100]. The C_5Me_5–OAr-ligated yttrium alkyl complex **35** (Ar = $C_6H_3^tBu_2$-2,6) has been synthesized by the reaction of $(C_5Me_5)Y(OAr)_2$ (**34**) with 1 equiv. of $KCH(SiMe_3)_2$ in hexane (Scheme 21) [101]. Hydrogenolysis of **35** with H_2 affords the hydride complex **36**. The reaction of $YCl_3(thf)_{3.5}$ with KC_5Me_5 followed by $Li(OEt_2)[PhC(NSiMe_3)_2]$ in THF gives the stable yttrium cyclopentadienyl–benzamidinate chloride complex $[(C_5Me_5)Y(PhC(NSiMe_3)_2)(\mu\text{-}Cl)]_2$, which upon reaction with 2 equiv. of MeLi in the presence of tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) affords the structurally characterized Me-bridged Y–Li heterobimetallic complex $(C_5Me_5)Y(PhC(NSiMe_3)_2)(\mu\text{-}Me)_2Li(tmeda)$ [102]. Oxidation of $(C_5^iPr_4H)Sm(\mu\text{-}I)(thf)_2]_2$ with 1 equiv. of *tert*-butylperoxide ${}^tBuOO{}^tBu$ yields the alkoxide complex $(C_5^iPr_4H)SmI(O^tBu)(thf)$ [38].

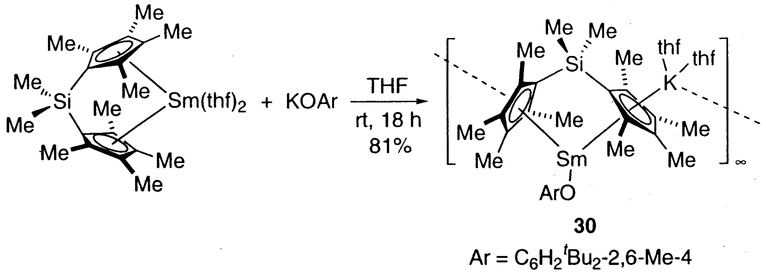


Scheme 20.

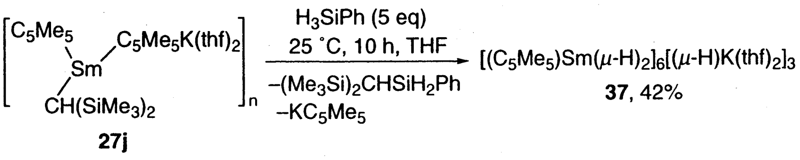


Scheme 21.

Alkane elimination reaction between $Y(CH_2SiMe_3)_3(THF)_2$ and $(C_5Me_4H)SiMe_2R$ (R = Me, Ph, C_6F_5) in pentane quantitatively gives the mono(cyclo-



Scheme 19.



Scheme 22.

pentadienyl) bis(alkyl) complex $(C_5Me_4SiMe_2R)Y(CH_2SiMe_3)_2(thf)$, which upon reaction with H_2 or $PhSiH_3$ yields a pentane-soluble complex with the probable formula $[(C_5Me_4SiMe_2R)YH_2]_4 \cdot 2thf$ (R = Me, Ph) [103]. The structurally characterized Sm(III)–K polyhydrido cluster complex **37**, which consists formally of six '$(C_5Me_5)SmH_2$' and three '$KH(thf)_2$' units, has been obtained by treatment of the (pentamethylcyclopentadienyl)samarium(II) alkyl complex **27j** with an excess of $PhSiH_3$ in THF (Scheme 22) [97]. The reaction of $Ln(BH_4)_3(thf)_3$ with 1 equiv. of $NaC_5H^iPr_4$ affords the mono(cyclopentadienyl) bis(borohydride) complexes $(C_5H^iPr_4)Ln(BH_4)_2(thf)$ (Ln = Nd, Sm) [104].

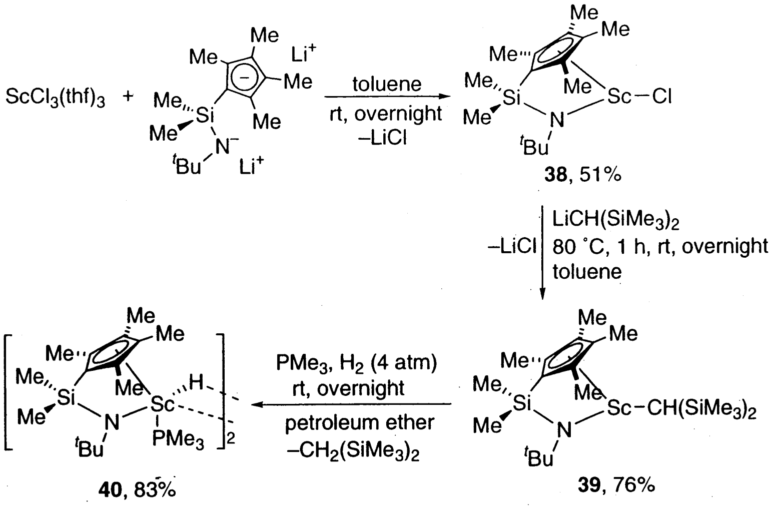
3.1.2. *Complexes bearing linked cyclopentadienyl–amido or –phosphido ligands*

The metathetical reaction between $ScCl_3(thf)_3$ and $Li_2[Me_2Si(C_5Me_4)N^tBu]$ in toluene yields the corresponding silylene-linked cyclopentadienyl–amido/chloride complex **38**, which upon alkylation with $LiCH(SiMe_3)_2$ affords the alkyl complex **39** (Scheme 23) [105]. Hydrogenolysis of **39** in the presence of PMe_3 yields the corresponding PMe_3-coordinated hydride complex **40**. The alkane elimination reaction between $Ln(CH_2SiMe_3)_3(thf)_2$ (Ln = Y, Yb, Lu) and $(C_5Me_4H)SiMe_2NH^tBu$ in pentane at 0 °C offers an excellent salt-free route to the linked cyclopentadienyl–amido lanthanide alkyl complexes **41a**–**c** (Scheme 24) [103,106,107]. The reaction of **41a**–**c** with H_2 or $PhSiH_3$ at room temperature easily gives the hydride complexes **42a**–**c**. The analogous scandium alkyl–hydride complexes with a donating amino group bonding to the cyclopentadienyl ring have also been prepared in a similar way [108]. A similar reaction between the bulkier alkyl complexes $Ln[CH(SiMe_3)_2]_3$ (Ln = Yb, Lu) with $(C_5Me_4H)SiMe_2(NH^tBu)$ requires reflux in toluene to afford $Me_2Si(C_5Me_4)(N^tBu)LnCH(SiMe_3)_2$ [109].

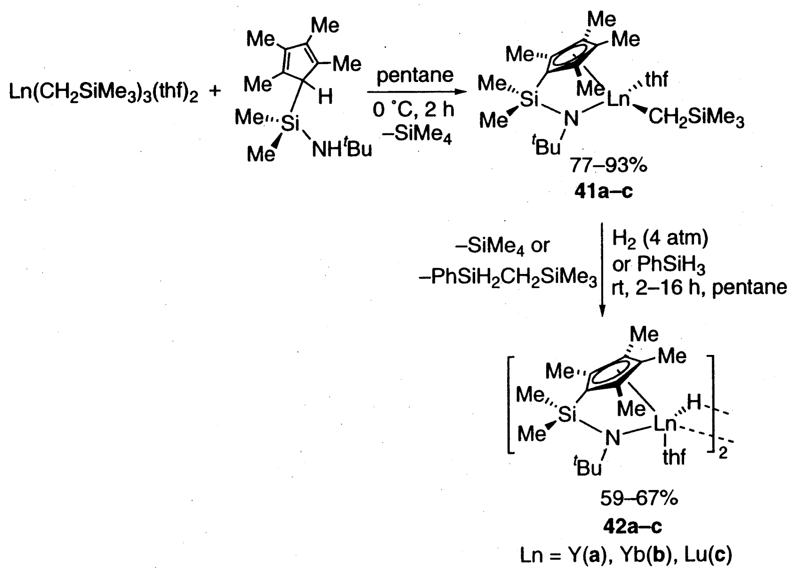
Attempts to use the silylene-linked cyclopentadienyl–*tert*-butylamido ligand $[Me_2Si(C_5Me_4)(N^tBu)]^{2-}$ for the synthesis of the analogous lanthanide(II) complexes have not yet been successful. The reaction between $SmI_2(thf)_2$ and $Li_2[Me_2Si(C_5Me_4)N^tBu]$ yielded an unidentified yellow, possibly Sm(III) compound, while the similar reaction with $YbI_2(thf)_2$ led to incorporation of LiI into the product [14,110]. The acid-base reaction between $(C_5Me_4H)SiMe_2NH^tBu$ and $Ln[N(SiMe_3)_2]_2(thf)_2$ resulted in metalation only at the cyclopentadienyl unit to give the metallocene complexes $Ln(C_5Me_4SiMe_2NH^tBu)_2$ (Ln = Sm, Yb) [14,110].

The use of the more protonic aniline derivatives such as $(C_5Me_4H)SiMe_2NHPh$ to react with $Ln[N(SiMe_3)_2]_2(thf)_2$ (Ln = Sm, Yb) has successfully afforded the corresponding cyclopentadienyl–anilido lanthanide(II) complexes **43a**,**b** (Scheme 25) [110]. Recrystallization of **43b** from toluene–hexane removed two of the three thf ligands and yielded a dimeric Yb(II) complex through 'intermolecular' Yb–Ph π-interactions, $[Me_2Si(C_5Me_4)(NPh)Yb(thf)]_2$.

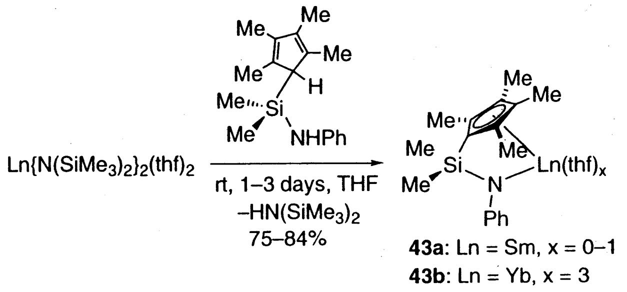
In contrast to numerous silylene-linked cyclopentadienyl–amido complexes of various metals



Scheme 23.



Scheme 24.

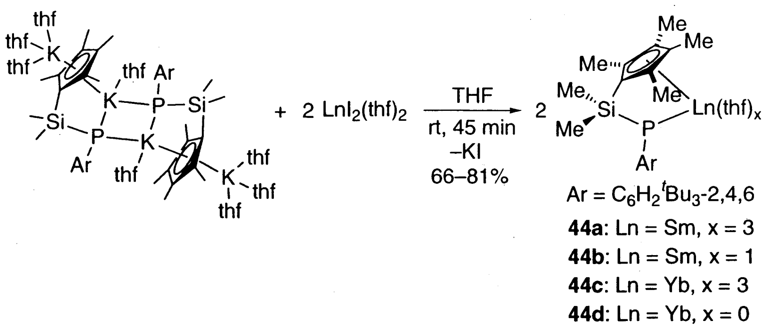


Scheme 25.

[12,111], the analogous phosphido compounds remain very rare because of easy cleavage of the P–Si bond [112]. Recent work in our laboratory has shown that lanthanide complexes bearing silylene-linked cyclopentadienyl–phosphido ligands are somewhat more stable than Group 4 metal analogues [113,114]. The metathetical reaction between $LnI_2(thf)_2$ (Ln = Sm, Yb) and $[Me_2Si(C_5Me_4)(PAr)K_2(thf)_4]_2$ readily affords the corresponding linked cyclopentadienyl–phosphido lanthanide(II) complexes **44a**–**d** (Scheme 26), Despite the intense distortion in the ligand [113]. These complexes are stable in the solid state at room temperature under an inert atmosphere, but gradually decompose into still unidentified products in a THF solution during a period of 1–3 days. Nevertheless, their reaction chemistry can be examined in THF or toluene [113].

3.2. Polymerization of ethylene

The cyclopentadienyl–anilido samarium(II) complex **43a** shows a moderate activity (44.8 g $mmol^{-1}$ h^{-1} atm^{-1}) for ethylene polymerization, affording linear polyethylene of high molecular weight ($M_n = 7.26 \times 10^5$) and narrow polydispersity ($M_w/M_n = 1.58$) [110]. The mixed-ligand effect is obvious on comparison of these results with those reported for the samarocene(II) complex $(C_5Me_5)_2Sm(thf)$ (5.06 g $mmol^{-1}$ h^{-1} atm^{-1}, $M_n < 2.5 \times 10^4$, $M_w/M_n = 2.28$) [34,49,95] and the bis(silylamido) samarium(II) complex $Sm[N(SiMe_3)_2]_2(thf)_2$ which is inert for ethylene polymerization under the same conditions [95]. The polymerization of ethylene by the mono(thf)-coordinated, cyclopentadienyl–phos-



Scheme 26.

phido samarium(II) complex **44b** (13.6 g mmol^{-1} h^{-1} atm^{-1}) yields an extremely high molecular-weight polymer that is insoluble in *ortho*-dichlorobenzene at 135 °C ($M_n > 4 \times 10^6$) [113]. In contrast, the tris(thf)-coordinated Sm(II) analogue **44a** does not show an activity for ethylene polymerization under the same conditions. These results suggest that creation of a sterically (or coordinatively) unsaturated metal center is essential for a polymerization reaction. However, the thf-free or mono(thf)-coordinated, less reducing Yb(II) complex **44d** or $[Me_2Si(C_5Me_4)(NPh)Yb(thf)]_2$ is inactive under the same conditions [110,113], suggesting that the present lanthanide(II)-promoted polymerization reactions is initiated by one-electron transfer from the Ln(II) center to an ethylene monomer. The silylene-linked cyclopentadienyl–amido yttrium(III) alkyl (**41a**) or hydride (**42a**) complexes shows a very low activity for the polymerization of ethylene, probably owing to the presence of the strongly coordinating thf ligand (**41a**: 0.21 g mmol^{-1} h^{-1} atm^{-1}; **42a**: 0.08 g mmol^{-1} h^{-1} atm^{-1}) [106]. The activity of the C_5Me_5–OAr-supported Y(III) hydride complex **36** is also very low possibly because of the strong μ-H-bridges [101]. The monocyclopentadienyl lanthanum dialkyl complex $(C_5Me_5)La(CH(SiMe_3)_2)_2(thf)$ (**33**·thf) is moderately active for ethylene polymerization at 25 °C (ca. 20 g mmol^{-1} h^{-1} atm^{-1}), yielding linear polyethylene with M_n up to 1.5×10^6 and $M_w/M_n = 1.28$–1.79 [115].

The C_5Me_5–ER-ligated-Sm(II) complexes **27a**–**e**,**g**,**j**, **28**, and **29a**, which bear the neutral 'C_5Me_5M' ligand (M = K or Na), all show good activity for the polymerization of ethylene at 25 °C under 1 atm, to give linear polyethylene with M_n up to 3×10^6 and $M_w/M_n = 1.64$–2.90) [95,97]. These unlinked, mixed-ligand-supported complexes are generally more active than the samarocene(II) complexes $(C_5Me_5)_2Sm(thf)_n$ ($n = 0$–2) as well as the silylene-linked cyclopentadienyl–anilido and –phosphido analogues **43a** and **44b**, probably owing to easy dissociation of the 'C_5Me_5M' ligand to generate an unsaturated, more flexible C_5Me_5–ER-ligated-Sm(II) center. The ER-ligand dependence of the reactivity in this series of complexes has also been observed. The 4-Me-2,6-$^tBu_2C_6H_2O$-ligated complex **27a** shows the highest activity (194 g mmol^{-1} h^{-1} atm^{-1}), while the $(Me_3Si)_2N$-ligated complex **27e** gives the highest molecular weight of polyethylene ($M_n = 3.1 \times 10^6$) [95]. In contrast to the highly reactive **27a**, the analogous complex **30**, whose two cyclopentadienyl units are linked by a silylene group, is inactive under the same conditions, probably owing to difficulty in the dissociation of the 'C_5Me_4K' unit from the Sm(II) center. The analogous, less reducing Yb(II) or Eu(II) complexes such as **27f**,**k**,**l** are again inactive. The Eu(II) and Yb(II) silyl complexes **27h**,**i** are, however, active for ethylene polymerization, which is probably initiated through migration of the SiH_3 group [96].

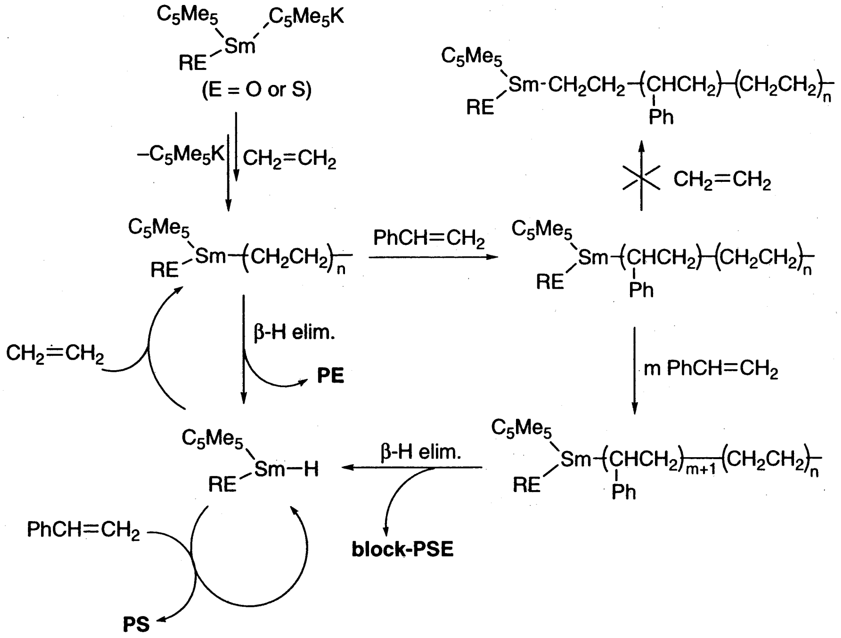
3.3. Polymerization of styrene

It has been shown that styrene can be inserted into the metal–hydride bond of the silylene-linked cyclopentadienyl–amido scandium or yttrium complex **40** or **42a**, but no polymerization occurs because of formation of stable allylic type complexes [105,106]. Upon partial loss of its thf ligand under vacuum, the alkyl-bridged dimeric yttrium complex $[Me_2Si(C_5Me_4)(N^tBu)Y(\mu\text{-}C_6H_{13})(thf)]_2$, which is formed by the reaction of **42a** with 1-hexene, shows an activity for the polymerization of styrene at 25 °C (24 h, 100% yield, 2 mol% cat.) to give atactic polystyrenes ($rr \approx 70\%$) with M_n up to 6.1×10^4 and $M_w/M_n = 1.10$–1.23 [106]. The monocyclopentadienyl lanthanum dialkyl complex $(C_5Me_5)La(CH(SiMe_3)_2)_2(thf)$ (**33**·thf) is found to be active for styrene polymerization at 50 °C (24 h, ca. 80% yield, 1 mol% cat.; $M_n < 1.6 \times 10^4$, $M_w/M_n \approx 1.6$, $rr \approx 50\%$) [115].

The C_5Me_5–ER-ligated-Sm(II) complexes **27a**–**e**,**g**,**j** all show high activity for the polymerization of styrene at room temperature, in striking contrast to the homoleptic type Sm(II) complexes $(C_5Me_5)_2Sm(THF)_n$ ($n = 0$ or 2), $Sm(OAr)_2(THF)_3$ ($Ar = C_6H_2^tBu_2$-2,6-Me-4), and $Sm(N(SiMe_3)_2)_2(THF)_2$, which are inactive for styrene polymerization under the same conditions [95–97]. In most cases, a quantitative conversion can be achieved in less than 1 h (0.14 mol% cat.), which affords atactic polystyrenes with M_n ranging from 8.2×10^4 to 3.5×10^5 and $M_w/M_n = 1.45$–2.45. The ER-ligand dependence of the activity is also observed. Complex **27b**, which bears the less sterically demanding 2,6-$^iPr_2C_6H_3O$ ligand, is more active than the 4-Me-2,6-$^tBu_2C_6H_2O$-ligated complex **27a**. The more electron-donating amide complexes **27d**,**e** shows higher activity than the aryloxide and thiolate complexes **27a**–**c** [95]. The analogous, less reducing Yb(II) or Eu(II) complexes **27f**,**k**,**l** do not show activity for styrene polymerization under same conditions. Therefore, as in the case of ethylene, styrene polymerization must also be initiated through the dissociation of the 'C_5Me_5K' unit from the Sm(II) center, followed by one-electron transfer from the C_5Me_5–ER-ligated-Sm(II) to a monomer.

3.4. Polymerization of 1-alkenes, dienes, and other monomers

The polymerization of 1-alkenes by the linked cyclopentadienyl–amido scandium hydride complex **40** affords atactic products of low molecular weight ($M_n = 3000$–7000) [105]. The stoichiometric reaction between **40** and propylene yields the phosphine-free, *n*-propyl-bridged scandium dimer $[Me_2Si(C_5Me_4)(N^tBu)Sc(\mu\text{-}^nPr)]_2$, which is considerably more active and affords higher molecular-weight polymers than the phosphine-coordinated complex **40** (at 25 °C, poly(1-pentene):



Scheme 27.

$M_n \approx 6000$, $M_w/M_n = 1.5$; polypropylene: $M_n \approx 9600$, $M_w/M_n = 1.8$) [105]. The analogous yttrium hydride complex **42a** does not effect 1-alkene polymerization, probably because of the presence of the strongly coordinating thf ligand [106,107].

The C_5Me_5–OAr-ligated yttrium hydride complex **36** is active for the polymerization of 1-hexene, yielding a polymer with $M_n = 9400$ and $M_w/M_n = 1.67$ [101]. Complex **36** can also effect catalytic cyclopolymerization of 1,5-hexadiene to give poly(methylene-1,3-cyclopentanediyl). Under the presence of MMAO as a cocatalyst, the linked cyclopentadienyl–phosphido samarium(II) complex **44b** effects the 1,4-*cis*-stereospecific polymerization of 1,3-butadiene (1,4-*cis*:1,4-*trans*:1,2- = 92.8:4.0:3.2; $M_n = 3.07 \times 10^5$, $M_w/M_n = 1.99$) [113], although its activity and stereoselectivity are not as high as those of the samarocene-based systems [61,62]. The polymerization of MMA, hexyl isocyanate, and acrylonitrile by the monocyclopentadienyl lanthanum dialkyl complex $(C_5Me_5)La(CH(SiMe_3)_2)_2(thf)$ (**33** · thf) [115] and the ring-opening polymerization of ε-caprolactone by the C_5Me_5–OAr-ligated dimeric–Sm(II) complex **26** [116] and the silylene-linked cyclopentadienyl–phosphido Sm(II) complex **44b** [113] have also been reported.

3.5. Block copolymerization of ethylene with styrene

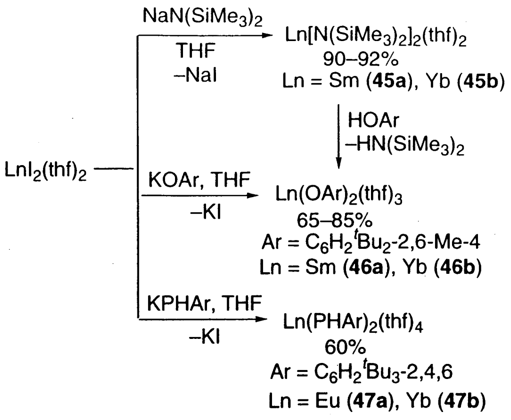
The mixed-ligand-supported Sm(II) complexes **27a**–**c** are active not only for the homopolymerization of ethylene and styrene, but also for the copolymerization of these two monomers, which affords styrene–ethylene block copolymers with M_n around 2×10^5 and $M_w/M_n = 1.60$–2.21 in the presence of both monomers (styrene, 3–10 ml; ethylene, 1 atm; 25 °C) [95,117]. Among these complexes, the thiolate complex **27c** shows the highest selectivity for the copolymerization reaction (89–96%). Homopolystyrene is usually the only byproduct while homopolyethylene is not formed, except when a very small amount of styrene monomer is introduced, which leads to formation of homopolyethylene as a dominant product. The polystyrene content in the copolymers increases almost linearly as the amount of styrene is increased under 1 atm of ethylene and can be easily adjusted within the entire range of 0–100%. Although extensive studies on the copolymerization of ethylene with styrene have been carried out with various catalytic systems including the Kaminsky catalysts [111], this is the first example of selective block-copolymerization of ethylene with styrene under the presence of both monomers.

In contrast with the aryloxide and thiolate complexes **27a**–**c**, the analogous amide complexes **27d**,**e**, which show much higher activity for styrene polymerization, yield homopolystyrene as the only or a major product under the presence of both monomers. On the other hand, the phosphide Sm(II) complex **28** and the 'C_5Me_5Na'-coordinated Sm(II) complex **29a**, which are much less active for styrene polymerization, affords only homopolyethylene under the similar conditions [95]. Sequential polymerization–copolymerization reactions of styrene with ethylene by **27b** have shown that the insertion of ethylene into the propagation site of a polystyrene unit does not take place, while the insertion of styrene into a polyethylene unit is possible [95,117]. These results suggest that the copolymerization reaction should begin with ethylene polymerization followed by successive styrene incorporation. It is obvious that a complex must show a well-balanced activity toward each monomer to accomplish selectively the copolymerization reaction under the presence of both monomers. A possible mechanism for the copolymerization to give styrene–ethylene block copolymers (PSE) is shown in Scheme 27 [60,95].

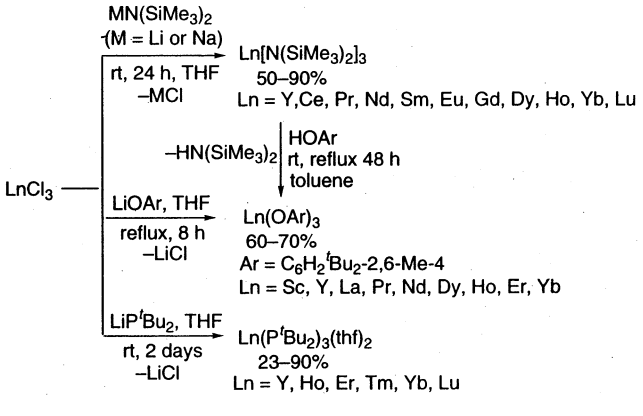
4. Cyclopentadienyl-free complexes

4.1. Synthesis

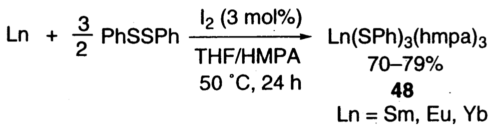
As alternatives to the cyclopentadienyl ancillary ligands in lanthanide polymerization catalysts, various monodentate and polydentate ligand systems, such as alkoxides or aryloxides [116,118–124], silylamides [125–130], thiolates [78,131,132], hydrotris(pyrazolyl)borates [133,134], benzamidinates [102,135,136], β-diketiminates [137], 1,5-diazapentadienyls [138], and iminomethylpyrrolyls [139], have been examined. In many cases, the synthetic methods for these complexes are analogous to those for the metallocene analogues.



Scheme 28.



Scheme 29.



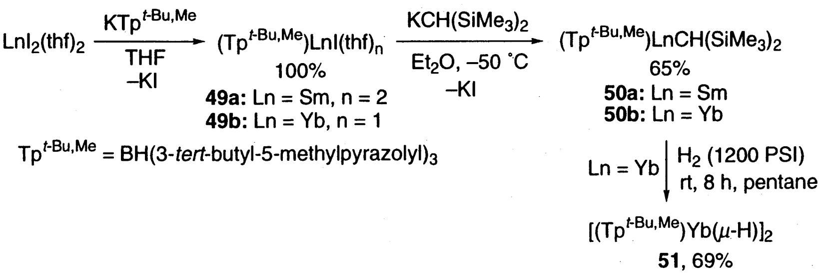
Scheme 30.

The metathetical reaction of $LnI_2(thf)_2$ with 2 equiv. of $NaN(SiMe_3)_2$ in THF gives straightforwardly the bis(silylamido)lanthanide(II) complexes $Ln[N(SiMe_3)_2]_2(thf)_2$ (Ln = Sm (**45a**), Yb (**45b**)) (Scheme 28) [119,125,140]. Similarly, the reaction of $LnI_2(thf)_2$ with 2 equiv. of KOAr (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4) or KPHAr (Ar = $C_6H_2{}^tBu_3$-2,4,6) affords the corresponding lanthanide(II) bis(aryloxide) complexes **46a,b** [118,141] or bis(phosphide) complexes **47a**,**b** [142], respectively. The acid-base reaction between **45a**,**b** and HOAr also provides a convenient route to the aryloxide complexes **46a,b** [118,141]. Trivalent lanthanide amide [126,127,143], aryloxide [144], and phosphide [145] complexes have been synthesized in an analogous way, as shown in Scheme 29.

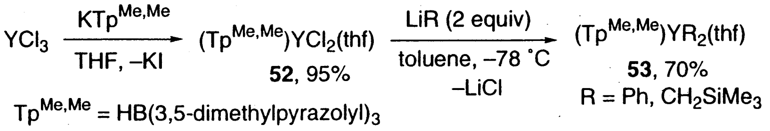
The reaction of metallic Ln with 1.5 equiv. of PhSSPh offers an convenient salt-free route to the lanthanide(III) trithiolate complexes $Ln(SPh)_3(hmpa)_3$ (**48**, Ln = Sm, Eu, Yb), as shown in Scheme 30 [131,132]. The use of excess Ln in this reaction affords the corresponding lanthanide(II) dithiolate complexes [131,132].

The reaction of $SmI_2(THF)_2$ with 2 equiv. of $NaTp^{Me,Me}$ ($Tp^{Me,Me}$ = HB(3,5-Me_2-pyrazolyl$)_3$) in THF yields immediately the corresponding samarium(II) bis(hydrotris(pyrazolyl)borate) complex $Sm(Tp^{Me,Me})_2$ as a THF-insoluble purple powder [146]. The reaction of $LnI_2(THF)_2$ (Ln = Sm or Yb) with 1 equiv. of $KTp^{^tBu,Me}$ ($Tp^{^tBu,Me}$ = HB(3-^{t}Bu-5-Me-pyrazolyl$)_3$) gives quantitatively the mono(hydrotris(pyrazolyl)borate) iodide complexes **49a**,**b**, which upon reaction with 1 equiv. of $KCH(SiMe_3)_2$ in diethyl ether at −50 °C yield the alkyl complexes **50a**,**b** (Scheme 31) [147,148]. A discrete $Tp^{^tBu,Me}$-supported ytterbium(II) hydrido complex (**51**) has been prepared by hydrogenolysis of the alkyl complex **50b** in pentane (Scheme 31) [134]. The yttrium(III) mono(hydrotris(pyrazolyl)borate) bis(hydrocarbyl) complexes (**53**) have been synthesized by the metathetical reaction between the dichloride complex **52** and 2 equiv. of LiR (R = Ph or CH_2SiMe_3), as shown in Scheme 32 [133].

The bis(benzamidinate)-ligated yttrium chloride complex **54**, which is prepared by the reaction of $YCl_3(thf)_{3.5}$ with 2 equiv. of $Li[PhC(NSiMe_3)_2]$, serves as a good precursor to the alkyl complex **55** (Scheme 33). Hydrogenolysis of **55** easily affords the hydride complex **56** [149]. Lanthanide complexes bearing the (alkoxysilyl)amido ligand $[Me_2Si(O^tBu)(N^tBu)]^-$ [129] and the bis(iminophosphorano)methanide ligand $[CH(Ph_2P=$



Scheme 31.



Scheme 32.

NSiMe$_3$)$_2$]$^-$ [150] can also be prepared analogously. The bis(diazapentadienyl)ytterbium(II) complex **57** has been isolated as red crystals from the reaction of YbBr$_2$ with 2 equiv. of K[(C$_5$H$_4$N)$_2$CPh] (Scheme 34) [138], while similar reaction of SmI$_2$ with K[(C$_5$H$_4$N)$_2$CPh] led to formation of an oily product containing impurities.

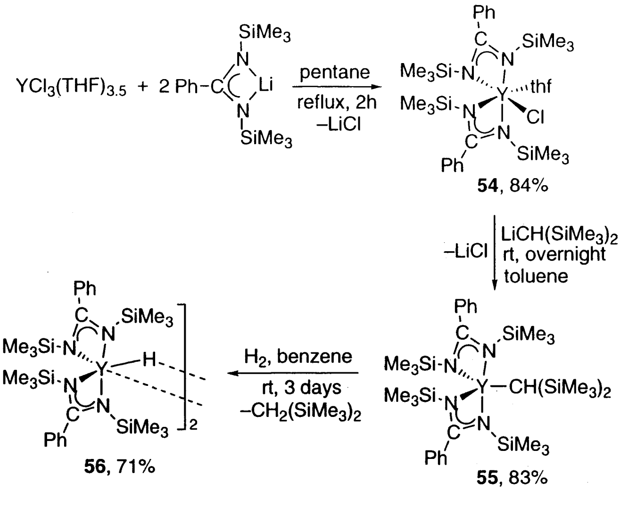
The amine elimination reaction between Y[N(SiMe$_3$)$_2$]$_3$ and 1 equiv. of 2,5-bis[*N*-(2,6-dimethylphenyl)iminomethyl]pyrrole (**58**) yields predominantly the mono(pyrrolyl) complex **59**, in which the pyrrolyl unit acts as a tridentate ligand (Scheme 35) [139]. In contrast, similar treatment of the bulkier 2,5-bis[*N*-(2,6-diisopropylphenyl)iminomethyl]pyrrole (**60**) with Y[N(SiMe$_3$)$_2$]$_3$ gives the bis(pyrrolyl) complex **61**, in which the pyrrolyl unit behaves as a bidentate ligand (Scheme 35). The acid-base reaction between Sm(NCy$_2$)$_3$ and CH$_2$(Ph$_2$P$=$NSiMe$_3$)$_2$ affords the samarium(III) bis(iminophosphorano) chelate complex **62** with a Sm$=$C bond (Scheme 36) [151].

The structurally characterized homoleptic alkyl lanthanide(II) complexes **63a**,**b** have been synthesized by the metathetical reaction of LnI$_2$ (Ln = Eu or Yb) with 2 equiv. of KC(SiMe$_3$)$_3$ in pentane (Scheme 37) [152,153]. Similarly, the reaction of LnCl$_3$ (Ln = Sc, Y, Tb, Er or Yb) with 3 equiv. of LiCH$_2$(SiMe$_3$) in THF affords the corresponding tris(alkyl) complexes (**64**) (Scheme 38) [106–108,154,155]. The homoleptic, salt-free tris[bis(trimethylsilyl)methyl] complexes (**65**) of Y(III) [156], La(III) [157], Sm(III) [157], and Lu(III) [156] have been synthesized by the reaction of the tris(aryloxide) complexes Ln(OAr)$_3$ (Ar = C$_6$H$_3^t$Bu$_2$-2,6) with 3 equiv. of LiCH(SiMe$_3$)$_2$ (Scheme 39). Similar reaction of LnCl$_3$ with LiCH(SiMe$_3$)$_2$ led to incorporation of LiCl into the products [158–160].

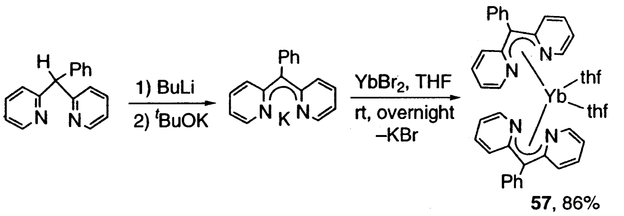
The reaction of NdCl$_3$ with allyllithium yields a ate complex, [Li(dioxane)][Nd(η^3-C$_3$H$_5$)$_4$] (**66**) [161], which upon reaction with BEt$_3$ gives the neutral allyl complex **67** (Scheme 40) [162].

4.2. Polymerization

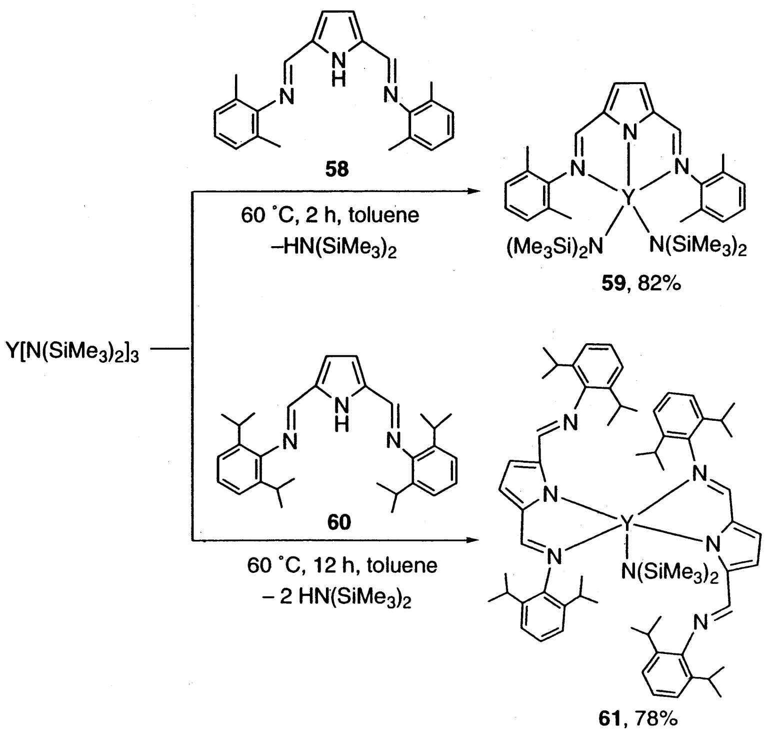
Very few Cp-free lanthanide complexes have been reported to show activity for olefin polymerization. The Tp$^{\text{Me,Me}}$-ligated yttrium bis(hydrocarbyl) complex such



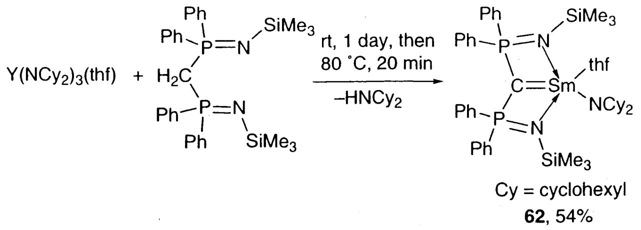
Scheme 33.



Scheme 34.



Scheme 35.



Scheme 36.

$$\mathrm{LnI_2 + 2\,KC(SiMe_3)_3 \xrightarrow[\substack{25\ ^\circ C,\ 48\ h\\ -KI}]{\text{pentane}} Ln[CH(SiMe_3)_2]_2}$$

65–85%

Ln = Eu (**63a**), Yb (**63b**)

Scheme 37.

$$\mathrm{LnCl_3 + 3\,LiCH_2SiMe_3 \xrightarrow[\substack{0\ ^\circ C,\ 3\ h\\ -LiCl}]{\text{THF/hexane}} Ln(CH_2SiMe_3)_3(thf)_2}$$

52–82%

Ln = Sc, Y, Tb, Er, Yb, Lu

64

Scheme 38.

$$\mathrm{Ln(OAr)_3 + 3\,LiCH(SiMe_3)_2 \xrightarrow[\substack{25\ ^\circ C,\ 30\ min\\ -LiOAr}]{\text{pentane}} Ln[CH(SiMe_3)_2]_3}$$

$\mathrm{Ar = C_6H_3{}^tBu_2\text{-}2,6}$

53–75%

Ln = Y, La, Sm, Lu

65

Scheme 39.

$$\mathrm{NdCl_3 + 4\,Li(C_3H_5)(C_4H_8O_2) \xrightarrow[-LiCl]{50\ ^\circ C,\ 8\ h} Li[Nd(C_3H_5)_4](C_4H_8O_2)_{1.5}}$$

66, 80%

$$\xrightarrow[\substack{50\ ^\circ C,\ 2\ h\\ -Li[BEt_3(C_3H_5)]}]{\mathrm{BEt_3}} \mathrm{Nd(C_3H_5)_3(C_4H_8O_2)}$$

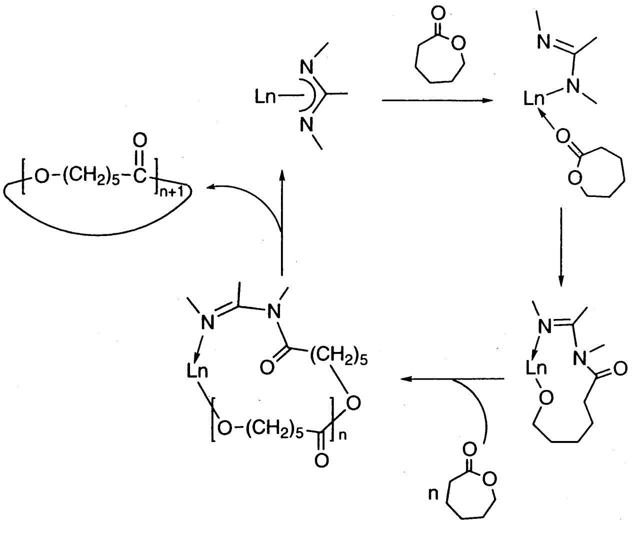
67, 90%

Scheme 40.

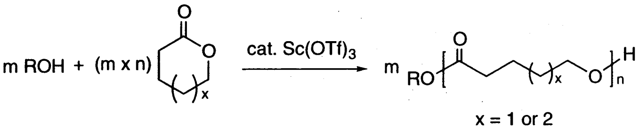
as **53** represents a rare example of a Cp-free single component catalyst that is active for ethylene polymerization, although the overall catalytic activity is very low (<1 g mmol^{-1} h^{-1} atm^{-1}) [133]. The combination of the neodymium *tert*-butoxide $\mathrm{Nd_3(\mu_3\text{-}O^tBu)_2(\mu\text{-}O^t\text{-}Bu)_3(O^tBu)_4(thf)_2}$ with 1 equiv. of a dialkylmagnesium reagent affords a catalyst for the pseudo-living polymerization of ethylene (ca. 10 g mmol^{-1} h^{-1} atm^{-1}) and ethylene–MMA block copolymerization [163]. The neutral allyl complex $\mathrm{Nd((\eta^3\text{-}C_3H_5)_4(C_4H_8O_2)}$ (**67**) is active for the polymerization of 1,3-butadiene with 1,4-*trans* selectivity [162]. By addition of a cocatalyst such as $\mathrm{Et_2AlCl}$, $\mathrm{EtAlCl_2}$, or MAO, however, a 1,4-*cis* selectivity of as high as 94% can be achieved [162]. Analogous 1,4-*cis* stereospecific polymerization of 1,3-butadiene by multi-component systems, such as $\mathrm{LnCl_3{-}AlEt_3{-}EtOH}$ [164], $\mathrm{AlEt_2Cl{-}Nd(OCOC_7H_{15})_3{-}Al({}^iBu)_3}$ [165], $\mathrm{Nd(\eta^3\text{-}C_3H_5)_2Cl{-}MAO}$ [166,167], and $\mathrm{(\eta^6\text{-}C_6H_5Me)Nd(AlCl_3Et)_3{-}AlH({}^iBu)_2}$ [168], has been extensively studied. Compared with the lanthanidocene-based catalysts [60–62], the Cp-free lanthanide systems usually produce polybutadienes with broader polydispersities and lower 1,4-*cis* selectivity.

Lanthanide thiolate complexes such as **48** can effect the syndiotactic polymerization of MMA through 1,4-addition of the SPh group to MMA [78]. Azaallyl or 1,5-diazapentadienyl lanthanide complexes, such as **57**, initiate the isotactic polymerization of MMA to give PMMA that showed a bimodal pattern in the GPC profile. The homoleptic bis(alkyl) ytterbium(II) complex $Yb[C(SiMe_3)_3]_2$ (**63b**) has proven to be an excellent initiator for the isotactic polymerization of MMA, which affords in high yield the isotactic PMMA (97%) with high molecular weight ($M_n = 5.0 \times 10^5$) and narrow polydispersity ($M_w/M_n = 1.1$) [169,170]. The MMA polymerization activity of the alkoxyphenyllanthanide(III) complexes $Ln[C_6H_3(O^iPr)_2\text{-}2,6]_3$ (Ln = Sm, Yb) is found to be very low [171].

A variety of Cp-free lanthanide compounds can initiate the ring-opening polymerization of lactones and lactide. Details can be found in recent more specialized reviews [172,173], and therefore, will not be further discussed here. Generally, a lanthanide isopropoxide species ($Ln-O^iPr$), either in isolated form (e.g. $(MeCOCHCOOEt)_2LnO^iPr$ (Ln = Y, Nd) [174], $Ln_5(\mu\text{-}O)(O^iPr)_{13}$ (Ln = Y, La, Sm, Yb) [175,176], $Y(O^iPr)_3$) [177] or generated in-situ (e.g. from reaction of $Ln(OAr)_3$ [121,122,178] or $Ln[N(SiMe_3)_2]_3$ [128] with ^iPrOH), can serve as an excellent initiator for the living polymerization–copolymerization of lactones or lactide. The reaction is initiated by nucleophilic attack of the O^iPr group on the monomer carbonyl carbon to give the thermodynamically favored ring-opened product. A lanthanide–nitrogen bond (Ln–N), such as that in $Yb[PhC(NSiMe_3)_2]_3$ [136,179] or **61** [139], can also initiate the ring-opening polymerization of ε-caprolactone, which in some cases yields cyclic polyesters, with regeneration of the initiator (Scheme 41) [82,136,179].



Scheme 41.



Scheme 42.

The most practically useful lanthanide compound for the ring-opening polymerization of lactones is perhaps scandium trifluoromethanesulfonate, $Sc(OTf)_3$, which can act as a catalyst for the living or controlled polymerization of ε-caprolactone, δ-valerolactone, and β-butyrolactone with an alcohol or H_2O as an initiator (Scheme 42) [180,181]). Linear polyesters with controlled molecular weights and narrow polydispersities (1.1–1.4) can be obtained in high yield. The lanthanide(III) tris(aryloxide) complexes $Ln(OAr)_3$ ($Ar = C_6H_2^tBu_2$-2,6-Me-4; Ln = Y, La, Nd, Dy) are reported to be highly active initiators for the ring-opening polymerization of 2,2-dimethyltrimethylene carbonate [124]. Polymerizations of cyclohexene oxide [182] and hexyl isocyanate [183] using lanthanide isopropoxides have also been described.

The use of SmI_2 [184] and other miscellaneous lanthanide compounds [185] in polymerization reactions has been recently reviewed, and will not be described here.

5. Conclusion and perspective

As described above, in contrast with the d-block transition metal Ziegler-Natta and Kaminsky polymerization catalysts, organolanthanide catalysts usually do not require a cocatalyst or activator to show high activity. However, in some cases (such as the samarocene-catalyzed 1,3-butadiene polymerization) the use of a cocatalyst may dramatically improve the activity of a lanthanide complex. Moreover, organolanthanide-based catalyst systems often show excellent living character and stereoselectivity, and can thus effect selective copolymerization of different monomers. The stereospecific living polymerization of MMA, the living polymerization of lactones and lactide, block copolymerization of nonpolar monomers with polar monomers, one-step block copolymerization of ethylene with styrene, and the 1,4-*cis* stereospecific living polymerization of 1,3-butadiene are among recent highlights, some of which are unique to the lanthanides.

It is also clear that the activity or behavior of a lanthanide complex in polymerization reactions can be tuned by modifying the ancillary ligands. Future challenges in this area will include the development of much more active, long-lived, single component ethylene and 1-alkene polymerization and copolymerization catalysts, single component stereoselective styrene polymerization catalysts, and polar–nonpolar monomer random copolymerization catalysts. In these endeavors, the design and creation of new lanthanide complexes with sophisticatedly controlled ligand environments will continue to play an important role.

References

[1] W.J. Evans, Polyhedron 6 (1987) 803.
[2] C.J. Schaverien, Adv. Organomet. Chem. 36 (1994) 283.
[3] F.T. Edelmann, in: E.W. Abel, F.G.A. Stone, G. Wilkinson, M.F. Lappert (Eds.), Comprehensive Organometallic Chemistry, vol. 4, Pergamon, Oxford, 1995, p. 11.
[4] H. Schumann, J.A. Meese-Marktscheffel, L. Esser, Chem. Rev. 95 (1995) 865.
[5] Z. Hou, Y. Wakatsuki, Science of Synthesis, In: R. Noyori, T. Imamoto (Eds.), Thieme, Stuttgart, Chapter 2.12.
[6] P.L. Watson, G.W. Parshall, Acc. Chem. Res. 18 (1985) 51.
[7] F.T. Edelmann, Top. Curr. Chem. 179 (1996) 247.
[8] R. Anwander, in: B. Cornils, W.A. Hermann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 2, VCH, Weinheim, 1996, p. 866.
[9] H. Yasuda, E. Ihara, Bull. Chem. Soc. Jpn. 70 (1997) 1745.
[10] S. Kobayashi (Ed.), Lanthanides: Chemistry and Use in Organic Synthesis, Springer, Berlin, 1999.
[11] F.T. Edelmann, Angew. Chem. Int. Ed. Engl. 34 (1995) 2466.
[12] J. Okuda, T. Eberle, in: A. Togni, R.L. Halterman (Eds.), Metallocenes, vol. 1, Wiley-VCH, Weinheim: Germany, 1998, p. 415.
[13] F. Nief, Eur. J. Inorg. Chem. 891 (2001).
[14] Z. Hou, Y. Wakatsuki, J. Organomet. Chem. 647 (2002) 61.
[15] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. 38 (1999) 428.
[16] J.L. Namy, P. Girard, H.B. Kagan, P.E. Caro, Nouv. J. Chim. 5 (1981) 479.
[17] R.E. Maginn, S. Manastyrskyj, M. Dubeck, J. Am. Chem. Soc. 85 (1963) 672.
[18] W.J. Evans, J.H. Meadows, W.E. Hunter, J.L. Atwood, J. Am. Chem. Soc. 106 (1984) 1291.
[19] W.J. Evans, J.W. Grate, H.W. Choi, I. Bloom, W.E. Hunter, J.L. Atwood, J. Am. Chem. Soc. 107 (1985) 941.
[20] G. Jeske, H. Lauke, H. Mauermann, P.N. Swepston, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8091.
[21] W.J. Evans, C.A. Seibel, J.W. Ziller, J. Am. Chem. Soc. 120 (1998) 6745.
[22] A.Z. Voskoboynikov, I.N. Parshina, A.K. Shestakova, K.P. Butin, I.P. Beletskaya, L.G. Kuz'mina, J.A.K. Howard, Organometallics 16 (1997) 4041.
[23] G. Jeske, L.E. Schock, P.N. Swepston, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8103.
[24] D. Stern, M. Sabat, T.J. Marks, J. Am. Chem. Soc. 112 (1990) 9558.
[25] (a) N. Höck, W. Oroschin, G. Paolucci, R.D. Fischer, Angew. Chem. Int. Ed. Engl. 25 (1986) 738;
(b) T. Akhnoukh, J. Muller, K. Qiao, X.F. Li, R.D. Fischer, J. Organomet. Chem. 408 (1991) 47.
[26] E. Bunel, B.J. Burger, J.E. Bercaw, J. Am. Chem. Soc. 110 (1988) 976.
[27] J.C. Yoder, M.W. Day, J.E. Bercaw, Organometallics 17 (1998) 4946.
[28] G.A. Molander, E.D. Dowdy, B.C. Noll, Organometallics 17 (1998) 3754.
[29] G. Desurmont, Y. Li, H. Yasuda, T. Maruo, N. Kanehisa, Y. Kai, Organometallics 19 (1811) 2000.
[30] M.H. Lee, J.-W. Hwang, Y. Kim, J. Kim, Y. Han, Y. Do, Organometallics 18 (1999) 5124.
[31] C. Qian, W. Nie, J. Sun, Organometallics 19 (2000) 4134.
[32] E.B. Coughlin, J.E. Bercaw, J. Am. Chem. Soc. 114 (1992) 7606.
[33] H. Yasuda, E. Ihara, Tetrahedron 51 (1995) 4563.
[34] E. Ihara, M. Nodono, K. Katsura, Y. Adachi, H. Yasuda, M. Yamagashira, H. Hashimoto, N. Kanehisa, Y. Kai, Organometallics 17 (1998) 3945.
[35] J.P. Mitchell, S. Hajela, S.K. Brookhart, K.I. Hardcastle, L.M. Henling, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 1045.
[36] M.A. Giardello, V.P. Conticello, L. Brard, M. Sabat, A.L. Rheingold, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10212.
[37] W.J. Evans, T.A. Ulibarri, J.W. Ziller, J. Am. Chem. Soc. 112 (1990) 2314.
[38] D. Barbier-Baudry, S. Heiner, M.M. Kubicki, E. Vigier, M. Visseaux, Organometallics 20 (2001) 4207.
[39] (a) W.J. Evans, L.R. Chamberlain, T.A. Ulibarri, J.W. Ziller, J. Am. Chem. Soc. 110 (1988) 6423;
(b) W.J. Evans, L.R. Chamberlain, J.W. Ziller, J. Am. Chem. Soc. 109 (1987) 7209.
[40] H. Yamamoto, H. Yasuda, K. Yokota, A. Nakamura, Chem. Lett. (1988) 1963.
[41] D.G.H. Ballard, A. Courtis, J. Holton, J. McMeeking, R. Pearce, J. Chem. Soc. Chem. Commun. (1978) 994.
[42] (a) B.J. Burger, M.E. Thompson, W.D. Cotter, J.E. Bercaw, J. Am. Chem. Soc. 112 (1990) 1566;
(b) P.J. Chirik, J.E. Bercaw, in: A. Togni, R.L. Halterman (Eds.), Metallocenes, vol. 1, Wiley-VCH, Weinheim, 1998, p. 111.
[43] (a) W.J. Evans, K.J. Forrestal, J.W. Ziller, J. Am. Chem. Soc. 120 (1998) 9273;
(b) W.J. Evans, K.J. Forrestal, J.W. Ziller, Angew. Chem. Int. Ed. Engl. 36 (1997) 774.
[44] E. Ihara, S. Yoshioka, M. Furo, K. Katsura, H. Yasuda, S. Mohri, N. Kanehisa, Y. Kai, Organometallics 20 (2001) 1752.
[45] S. Bogaert, T. Chenal, A. Mortreux, G. Nowogrocki, C.W. Lehmann, J.-F. Carpentier, Organometallics 20 (2001) 199.
[46] K. Koo, P.-F. Fu, T.J. Marks, Macromolecules 32 (1999) 981.
[47] S.N. Ringelberg, A. Meetsma, B. Hessen, J.H. Teuben, J. Am. Chem. Soc. 121 (1999) 6082.
[48] W.J. Evans, D.M. DeCoster, J. Greaves, Macromolecules 28 (1995) 7929.
[49] W.J. Evans, R.A. Keyer, J.W. Ziller, J. Organomet. Chem. 394 (1990) 87.
[50] W.J. Evans, T.A. Ulibarri, J.W. Ziller, J. Am. Chem. Soc. 112 (1990) 219.
[51] Y. Zhang, Z. Hou, Y. Wakatsuki, Macromolecules 32 (1999) 939.
[52] Y.X. Cheng, Q. Shen, Chin. Chem. Lett. 4 (1993) 743.
[53] F. Yuan, Q. Shen, J. Sun, J. Organomet. Chem. 538 (1997) 241.
[54] S.Y. Knjazhanski, E.S. Kalyuzhunaya, L.S.E. Herrera, B.M. Bulychev, A.V. Khvostov, A.I. Sizov, J. Organomet. Chem. 531 (1997) 19.
[55] S. Bogaert, J.-F. Carpentier, T. Chenal, A. Mortreux, G. Ricart, Macromol. Chem. Phys. 201 (1813) 2000.
[56] C.P. Casey, T.-Y. Lee, J.A. Tunge, D.W. Carpenetti II, J. Am. Chem. Soc. 123 (2001) 10762.
[57] C.P. Casey, J.F. Klein, M.A. Fagan, J. Am. Chem. Soc. 122 (2000) 4320.
[58] C.P. Casey, S.L. HallenBeck, J.M. Wright, C.R. Landis, J. Am. Chem. Soc. 119 (1997) 9680.
[59] L. Jia, X. Yang, A.M. Seyam, I.D.L. Albert, P.-F. Fu, S. Yang, T.J. Marks, J. Am. Chem. Soc. 118 (1996) 7900.
[60] Z. Hou, S. Kaita, Y. Wakatsuki, Pure Appl. Chem. 73 (2001) 291.

[61] S. Kaita, Z. Hou, Y. Wakatsuki, Macromolecules 32 (1999) 9078.
[62] S. Kaita, Z. Hou, Y. Wakatsuki, Macromolecules 34 (2001) 1539.
[63] D. Baudry-Barbier, N. Andre, A. Dormond, C. Pardes, P. Richard, M. Visseaux, C.J. Zhu, Eur. J. Inorg. Chem. (1998) 1721.
[64] W.E. Piers, P.J. Shapiro, E.E. Bunel, J.E. Bercaw, Synlett (1990) 74.
[65] H. Yasuda, H. Yamamoto, K. Yokota, S. Miyake, A. Nakamura, J. Am. Chem. Soc. 114 (1992) 4908.
[66] H. Yasuda, H. Yamamoto, M. Yamashita, K. Yokota, A. Nakamura, S. Miyake, Y. Kai, N. Kanehisa, Macromolecules 26 (1993) 7134.
[67] E. Ihara, M. Morimoto, H. Yasuda, Macromolecules 28 (1995) 7886.
[68] M.A. Giardello, Y. Yamamoto, L. Bard, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 3276.
[69] C. Qian, G. Zou, Y. Chen, J. Sun, Organometallics 20 (2001) 3106.
[70] L. Mao, Q. Shen, J. Polym. Sci. A: Polym. Chem. 36 (1998) 1593.
[71] L. Mao, Q. Shen, J. Sun, J. Organomet. Chem. 566 (1998) 9.
[72] L.S. Boffa, B.M. Novak, Macromolecules 30 (1997) 3494.
[73] L.S. Boffa, B.M. Novak, J. Mol. Catal. A: Chem. 133 (1998) 123.
[74] L.S. Boffa, B.M. Novak, Tetrahedron 53 (1997) 15367.
[75] S.Y. Knjazhanski, L. Elizalde, G. Cadenas, B.M. Bulychev, J. Polym. Sci. A: Polym. Chem. 36 (1998) 1599.
[76] S.Y. Knjazhanski, L. Elizalde, G. Cadenas, B.M. Bulychev, J. Organomet. Chem. 568 (1998) 33.
[77] M. Nodono, T. Tokimitsu, S. Tone, T. Makino, A. Yanagase, Macromol. Chem. Phys. 201 (2000) 2282.
[78] Y. Nakayama, T. Shibahara, H. Fukumoto, A. Nakamura, K. Mashima, Macromolecules 29 (1996) 8014.
[79] M. Yamashita, Y. Takemoto, E. Ihara, H. Yasuda, Macromolecules 29 (1996) 1798.
[80] W.J. Evans, H. Katsumata, Macromolecules 27 (1994) 2330.
[81] W.J. Evans, H. Katsumata, Macromolecules 27 (1994) 4011.
[82] K.C. Hultzsch, T.P. Spaniol, J. Okuda, Organometallics 16 (1997) 4845.
[83] B.-J. Deelman, E.A. Bijpost, J.H. Teuben, J. Chem. Soc. Chem. Commun. (1995) 1741.
[84] S.-y. Onozawa, T. Sakakura, M. Tanaka, Chem. Lett. (1994) 531.
[85] L. Mao, Q. Shen, M. Xue, Organometallics 16 (1997) 3711.
[86] Y. Wang, Q. Shen, L. Wu, Y. Zhang, J. Sun, J. Organomet. Chem. 626 (2001) 176.
[87] C.M. Forsyth, S.P. Nolan, T.J. Marks, Organometallics 10 (1991) 2543.
[88] W.J. Evans, D.M. DeCoster, J. Greaves, Organometallics 15 (1996) 3210.
[89] M. Visseaux, D. Barbier-Baudry, F. Bonnet, A. Dormond, Macromol. Chem. Phys. 202 (2001) 2485.
[90] H. Yasuda, M. Furo, H. Yamamoto, A. Nakamura, S. Miyake, N. Kibino, Macromolecules 25 (1992) 5115.
[91] G. Desurmont, T. Tokimitsu, H. Yasuda, Macromolecules 33 (2000) 7679.
[92] G. Desurmont, M. Tanaka, Y. Li, H. Yasuda, T. Tokimitsu, S. Tone, A. Yanagase, J. Polym. Sci. A: Polym Chem. 38 (2000) 4095.
[93] R. Nomura, Y. Shibasaki, T. Endo, J. Polym. Sci. A: Polym. Chem. 336 (1998) 2209.
[94] Z. Hou, Y. Zhang, T. Yoshimura, Y. Wakatsuki, Organometallics 16 (1997) 2963.
[95] Z. Hou, Y. Zhang, H. Tezuka, P. Xie, O. Tardif, T. Koizumi, H. Yamazaki, Y. Wakatsuki, J. Am. Chem. Soc. 122 (2000) 10533.
[96] Z. Hou, Y. Zhang, Y. Wakatsuki, unpublished result.
[97] Z. Hou, Y. Zhang, O. Tardif, Y. Wakatsuki, J. Am. Chem. Soc. 123 (2001) 9216.
[98] P.N. Hazin, J.C. Huffman, J.W. Bruno, Organometallics 6 (1987) 23.
[99] H. van den Heijden, C.J. Schaverien, A.G. Orpen, Organometallics 8 (1989) 255.
[100] H.J. Heeres, A. Meetsma, J.H. Teuben, R.D. Rogers, Organometallics 8 (1989) 2637.
[101] C.J. Schaverien, Organometallics 13 (1994) 69.
[102] R. Duchateau, A. Meetsma, J.H. Teuben, Organometallics 15 (1996) 1656.
[103] K.C. Hultzsch, T.S. Spaniol, J. Okuda, Angew. Chem. Int. Ed. 38 (1999) 227.
[104] D. Barbier-Baudry, O. Blacque, A. Hafid, A. Nyassi, H. Sitzmann, M. Visseaux, Eur. J. Inorg. Chem. (2000) 2333.
[105] P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 116 (1994) 4623.
[106] K.C. Hultzsch, P. Voth, K. Beckerle, T.P. Spaniol, J. Okuda, Organometallics 19 (2000) 228.
[107] S. Arndt, P. Voth, T.P. Spaniol, J. Okuda, Organometallics 19 (2000) 4690.
[108] Y. Mu, W.E. Piers, D.C. MacQuarrie, M.J. Zaworotko, V.G. Young, Jr., Organometallics 15 (1996) 2720.
[109] S. Tian, V.M. Arredondo, C.L. Stern, T.J. Marks, Organometallics 18 (1999) 2568.
[110] Z. Hou, T. Koizumi, M. Nishiura, Y. Wakatsuki, Organometallics 20 (2001) 3323.
[111] A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2578.
[112] T. Koch, S. Blaurock, F.B. Somoza, A. Voigt, R. Kirmse, E. Hey-Hawkins, Organometallics 19 (2000) 2556.
[113] O. Tardif, Z. Hou, M. Nishiura, T. Koizumi, Y. Wakatsuki, Organometallics 20 (2001) 4565.
[114] Z. Hou, O. Tardif, Y. Wakatsuki, unpublished result.
[115] K. Tanaka, M. Furo, E. Ihara, H. Yasuda, J. Poly. Sci. A: Polym. Chem. 39 (2001) 1382.
[116] M. Nishiura, Z. Hou, T. Imamoto, Y. Wakatsuki, Macromolecules 32 (1999) 8245.
[117] Z. Hou, J. Synth. Org. Chem. Jpn. 59 (2001) 82.
[118] Z. Hou, A. Fujita, T. Yoshimura, A. Jesorka, Y. Zhang, H. Yamazaki, Y. Wakatsuki, Inorg. Chem. 35 (1996) 7190.
[119] Z. Hou, A. Fujita, Y. Zhang, T. Miyano, H. Yamazaki, Y. Wakatsuki, J. Am. Chem. Soc. 120 (1998) 754.
[120] P.B. Hitchcock, M.F. Lappert, A. Singh, Inorg. Synth. 27 (1990) 164.
[121] W.M. Stevels, M.J.K. Ankone, P.J. Dijkstra, J. Feijen, Macromolecules 29 (1996) 8296.
[122] W.M. Stevels, M.J.K. Ankone, P.J. Dijkstra, J. Feijen, Macromolecules 29 (1996) 6123.
[123] B.M. Chamberlain, Y. Sun, J.R. Hagadorn, E.W. Hemmesch, J.V.G. Young, M. Pink, M.A. Hillmyer, W.B. Tolman, Macromolecules 32 (1999) 2400.
[124] J. Ling, Z. Shen, Q. Huang, Macromolecules 34 (2001) 7613.
[125] W.J. Evans, D.K. Frummond, H. Zhang, J.L. Atwood, Inorg. Chem. 27 (1988) 575.
[126] D.C. Bradley, J.S. Ghotra, F.A. Hart, J. Chem. Soc. Dalton Trans. (1973) 1021.
[127] W.A. Herrmann, R. Anwander, M. Kleine, W. Scherer, Chem. Ber. 125 (1971) 1992.
[128] E. Martin, P. Dubois, R. Jerome, Macromolecules 33 (2000) 1530.
[129] R. Duchateau, T. Tuinstra, E.A.C. Brussee, A. Meetsma, P. Th. van Duijnen, J.H. Teuben, Organometallics 16 (1997) 3511.
[130] M.D. Fryzuk, T.S. Haddad, S.J. Rettig, Organometallics 10 (1991) 2026.
[131] K. Mashima, Y. Nakayama, T. Shibahara, H. Fukumoto, A. Nakamura, Inorg. Chem. 35 (1996) 93.

[132] K. Mashima, A. Nakamura, J. Chem. Soc. Dalton Trans. (1999) 3899.

[133] D.P. Long, P.A. Bianconi, J. Am. Chem. Soc. 118 (1996) 12453.

[134] G.M. Ferrence, R. McDonald, J. Takats, Angew. Chem. Int. Ed. 38 (1999) 2233.

[135] R. Duchateau, C.T. van Wee, J.H. Teuben, Organometallics 15 (1996) 2291.

[136] D. Barbier-Baudry, A. Bouazza, C.H. Brachais, A. Dormond, M. Visseaux, Macromol. Rapid Commun. 21 (2000) 213.

[137] L.W.M. Lee, W.E. Piers, M.R.J. Elsegood, W. Clegg, M. Parvez, Organometallics 18 (1999) 2947.

[138] E. Ihara, K. Koyama, H. Yasuda, N. Kanehisa, Y. Kai, J. Organomet. Chem. 574 (1999) 40.

[139] Y. Matsuo, K. Mashima, K. Tani, Organometallics 20 (2001) 3510.

[140] T.D. Tilley, R.A. Andersen, A. Zalkin, J. Am. Chem. Soc. 104 (1982) 3725.

[141] J.R. van den Hende, P.B. Hitchcock, S.A. Holmes, M.F. Lappert, W.-P. Leung, T.C.W. Mak, S. Prashar, J. Chem. Soc. Dalton Trans. (1995) 1427.

[142] G.W. Rabe, I.A. Guzei, A.L. Rheingold, Inorg. Chem. 36 (1997) 4914.

[143] L.R. LaDuca, P.T. Wolczanski, Inorg. Chem. 31 (1992) 1311.

[144] M.F. Lappert, A. Singh, R.G. Smith, H.A. Stecher, A. Sen, Inorg. Synth. 27 (1990) 164.

[145] H. Schumann, G.-M. Frisch, Z. Naturforsch 34b (1979) 748.

[146] J. Takats, X.W. Zhang, V.W. Day, T.A. Eberspacher, Organometallics 12 (1993) 4286.

[147] L. Hasinoff, J. Takats, X.W. Zhang, J. Am. Chem. Soc. 116 (1994) 8833.

[148] G.H. Maunder, A. Sella, D.A. Tocher, J. Chem. Soc. Chem. Commun. (1994) 2689.

[149] R. Duchateau, C.T. van Wee, A. Meetsma, P. Th. van Duijnen, J.H. Teuben, Organometallics 15 (1996) 2279.

[150] M.T. Gamer, S. Dehnen, P.W. Roesky, Organometallics 20 (2001) 4230.

[151] K. Aparna, M. Ferguson, R.G. Cavell, J. Am. Chem. Soc. 122 (2000) 726.

[152] C. Eaborn, P.B. Hitchcock, K. Izod, J.D. Smith, J. Am. Chem. Soc. 116 (1994) 12071.

[153] C. Eaborn, P.B. Hitchcock, K. Izod, Z.-R. Lu, J.D. Smith, Organometallics 15 (1996) 4783.

[154] M.F. Lappert, R. Pearce, J. Chem. Soc. Chem. Commun. (1973) 126.

[155] J.L. Atwood, W.E. Hunter, R.D. Rogers, J. Holton, J. McMeeking, R. Pearce, M.F. Lappert, J. Chem. Soc. Chem. Commun. (1978) 140.

[156] C.J. Schaverien, A.G. Orpen, Inorg. Chem. 30 (1991) 4968.

[157] P.B. Hitchcock, M.F. Lappert, R.G. Smith, R.A. Barlett, P.P. Power, J. Chem. Soc. Chem. Commun. (1988) 1007.

[158] G.K. Barker, M.F. Lappert, J. Organomet. Chem. 76 (1974) C45.

[159] J.L. Atwood, M.F. Lappert, R.G. Smith, H. Zhang, J. Chem. Soc. Chem. Commun. (1988) 1308.

[160] C.J. Schaverien, J.B. van Mechelen, Organometallics 10 (1991) 1704.

[161] R. Taube, S. Maiwald, J. Sieler, J. Organomet. Chem. 513 (1996) 37.

[162] R. Taube, H. Windisch, S. Maiwald, H. Hemling, H. Schumann, J. Organomet. Chem. 513 (1996) 49.

[163] J. Gromada, T. Chenal, A. Mortreux, J.W. Ziller, F. Leising, J.-F. Carpentier, Chem. Commun. (2000) 2183.

[164] Z. Shen, Inorg. Chim. Acta 140 (1987) 7.

[165] L. Porri, G. Ricci, A. Giarrusso, N. Shubin, Z. Lu, ACS Symp. Ser. 749 (2000) 15.

[166] S. Maiwald, R. Taube, H. Hemling, H. Schumann, J. Organomet. Chem. 552 (1998) 195.

[167] R. Taube, H. Windsch, S. Maiwald, Macromol. Symp. 89 (1995) 393.

[168] P. Biagini, G. Lugli, L. Abis, R. Millini, New J. Chem. 19 (1995) 713.

[169] H. Yasuda, J. Polym. Sci. Part A: Polym Chem. 39 (1955) 2001.

[170] H. Yasuda, E. Ihara, Y. Nitto, T. Kakehi, M. Morimoto, M. Nodono, ACS Symp. Ser. 704 (1998) 149.

[171] E. Ihara, Y. Adachi, H. Yasuda, H. Hashimoto, N. Kanehisa, Y. Kai, J. Organomet. Chem. 569 (1998) 147.

[172] S. Agarwal, C. Mast, K. Dehnicke, A. Greiner, Macromol. Rapid Commun. 21 (2000) 195.

[173] B.J. O'Keefe, M.A. Hillmyer, W.B. Tolman, J. Chem. Soc. Dalton Trans. (2001) 2215.

[174] Y. Shen, Z. Shen, Y. Zhang, K. Yao, Macromolecules (1996) 8289.

[175] W.M. Stevels, M.J.K. Ankone, P.J. Dijkstra, J. Feijen, Macromol. Chem. Phys. 196 (1995) 1153.

[176] V. Simic, N. Apassky, L.G. Hubert-Pfalzgraf, Macromolecules 30 (1997) 7338.

[177] X. Deng, Z. Zhu, C. Xiong, L. Zhang, J. Appl. Polym. Sci. 64 (1997) 1295.

[178] W.M. Stevels, M.J.K. Ankone, P.J. Dijkstra, J. Feijen, Macromolecules 29 (1996) 3332.

[179] M. Visseaux, A.-H. Brachais, C. Boisson, K. Tortosa, C. R. Acad. Sci. Ser IIc: Chim 3 (2000) 631.

[180] N. Nomura, A. Taira, T. Tomioka, M. Okada, Macromolecules 33 (2000) 1497.

[181] M. Möller, R. Kange, J.L. Hedrick, J. Polym. Sci. A: Polym. Chem. 38 (2000) 2067.

[182] M. Thiam, N. Spassky, Macromol. Chem. Phys. 200 (1999) 2107.

[183] N. Fukuwatari, H. Sugimoto, S. Inoue, Macromol. Rapid Commun. 17 (1996) 1.

[184] R. Nomura, T. Endo, Chem. Eur. J. 4 (1998) 1605.

[185] E.N. Kirillov, E.A. Fedorova, A.A. Trifonov, M.N. Bochkarev, Appl. Organomet. Chem. 15 (2001) 151.