

Review

# Nonbridged half-metallocenes containing anionic ancillary donor ligands: New promising candidates as catalysts for precise olefin polymerization

Kotohiro Nomura\*, Jingyu Liu, Sudhakar Padmanabhan, Boonyarach Kitiyanan

*Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0101, Japan*

Received 26 September 2006; received in revised form 27 October 2006; accepted 1 November 2006

Available online 10 November 2006

## Abstract

Recent examples for synthesis of group 4 transition metal (Ti, Zr, Hf) complexes, especially nonbridged half-metallocenes containing anionic donor ligands of the type,  $Cp'MX_2(L)$  ( $Cp'$  = cyclopentadienyl group;  $M = Ti, Zr, Hf$ ;  $X = \text{halogen, alkyl etc.}$ ;  $L = \text{anionic donor ligands}$ ), as catalysts for precise olefin polymerization have been reviewed. It has been revealed that these complex catalysts displayed unique characteristics especially for ethylene copolymerizations and some examples are known to produce new polyolefins that cannot be prepared by ordinary catalysts such as classical Ziegler–Natta, metallocenes. Modification of both cyclopentadienyl fragment and anionic ancillary donor ligands are the key for precise olefin (co)polymerization.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Titanium; Zirconium; Hafnium; Olefin polymerization; Ligand effect; Half-metallocene

## Contents

1. Introduction	1
2. Nonbridged half-metallocenes	3
2.1. Olefin polymerization by half-titanocenes containing aryloxo ligands	4
2.2. Olefin polymerization by half-titanocenes containing various anionic ancillary donor ligands	8
2.3. Some chemistry related to olefin polymerization using half-titanocenes	15
2.4. Isospecific living polymerization of $\alpha$ -olefins and the related chemistry	17
2.5. Modification of ligands for syndiospecific styrene polymerization	18
3. Some ethylene copolymerizations by nonbridged half-titanocenes	21
3.1. Ethylene/ $\alpha$ -olefin copolymerization	21
3.2. Copolymerization of ethylene with styrene	22
3.3. Copolymerization of ethylene with cyclic olefin	24
4. Summary and outlook	25
Acknowledgements	25
References	26

## 1. Introduction

Polyolefin has been one of the most important commercial synthetic polymers in our daily life, and the market capacity

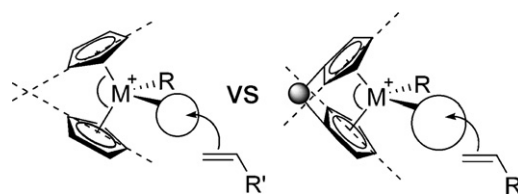
is still increasing even in the conventional polyolefins such as polyethylene (HDPE, LLDPE), polypropylene (PP). Recently, considerable attention has been paid to produce new polyolefins with specified function such as optical materials by COC (cyclic olefin copolymer), alternatives for poly(vinyl chloride) by ethylene/styrene copolymer and others. This is also due to that the use of polyolefins should be considered (especially from the aspect of contribution in the reduction of undesirable by-product

\* Corresponding author. Tel.: +81 743 72 6041; fax: +81 743 72 6049.  
E-mail address: [nomurak@ms.naist.jp](mailto:nomurak@ms.naist.jp) (K. Nomura).

and/or waste), because the recycling should be easier than the other specified polymers and the monomer synthesis step should be shorter than the other functionalized monomers. It is highly believed that the design of efficient transition metal complex catalysts that precisely control olefin coordination polymerization is the key for evolution of new polyolefins that have never been prepared by conventional catalysts. Therefore, research concerning design of efficient transition metal complex catalysts for controlled precise olefin polymerization have attracted considerable attention not only in the field of catalysis, organometallic chemistry, but also in the field of polymer chemistry [1–9]. Recent progress in the newly designed catalysts has offered the new possibility for evolution of new polymers, as described below [1–9].

It has been highly believed that the important key issues for a successful design of an efficient transition metal catalyst for ethylene (co)polymerizations are as follows: (a) catalytic activity, (b) molecular weight and molecular weight distribution, (c) comonomer (e.g.  $\alpha$ -olefin, styrene, cyclic olefins, etc.) incorporation, (d) others such as branching (short, long), structure/performance relationship. In particular, the catalysts exhibiting both better comonomer incorporations and remarkable catalytic activities are potentially important, because new polymers would be prepared by the copolymerization with new monomers (like so called traditionally unreactive comonomer in transition metal catalyzed coordination polymerization) in most cases. It has been reported that bridged (*ansa*) metallocene-type complexes show better comonomer incorporation than the nonbridged (unbridged) analogues in ethylene/ $\alpha$ -olefin copolymerization [1], although both steric and electronic factors were affected toward the catalytic activity and molecular weight for resultant polymers in ethylene polymerization by substituted zirconocenes [10]. The fact has been explained as that the bridged metallocenes possess rather large coordination space compared to the nonbridged analogues, allowing better accessibility for (rather) bulky  $\alpha$ -olefins (Scheme 1) [1–4,11–12].

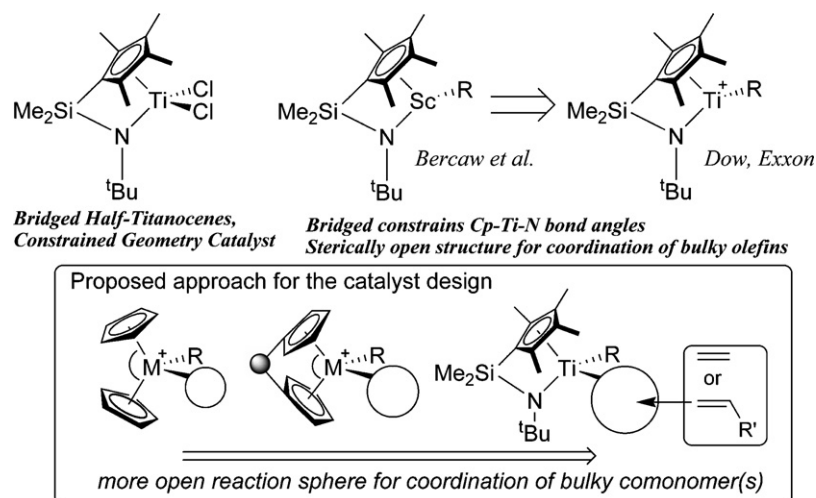
It has been well known that the linked amido-cyclopentadienyl titanium complex catalysts, so called “constrained geometry catalyst (CGC)”, showed efficient comonomer incor-



Scheme 1. Explanative drawings that bridged metallocenes show better comonomer incorporations than unbridged metallocenes in ethylene/ $\alpha$ -olefin copolymerization due to the more open space for coordination of bulky comonomer [1].

poration (Scheme 2) [4–5,13]. This complex was designed according to the analogous scandium complex reported by Bercaw et al. [14], and the reason for better comonomer incorporation has been explained as that the bridge constrains more open Cp–Ti–N bond angle offering better comonomer incorporation by allowing improved accessibility for (rather) bulky  $\alpha$ -olefin comonomers [4–5]. As summarized in Table 1 [15,16], the efficiency in  $\alpha$ -olefin in ethylene/ $\alpha$ -olefin copolymerization can be evaluated by  $r_E$  values ( $r_E = k_{EE}/k_{EO}$ , E = ethylene, O = 1-octene, etc.) in the copolymerization of ethylene with  $\alpha$ -olefin such as 1-hexene, 1-octene, and the  $r_E$  value decreases in the order:  $\text{Cp}_2\text{ZrCl}_2 \gg \text{rac-Me}_2\text{Si}[\text{benz(e)Ind}]_2\text{ZrCl}_2 > [\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ . These facts clearly support the above assumption that “the bridge constrains more open coordination sphere for bulky  $\alpha$ -olefins,” although recent results suggested that coordination sphere is not the exclusive factor for the better comonomer incorporation [17–19]. The  $r_E$  values were dependent upon the polymerization temperature, whereas the  $r_E \cdot r_O$  values were ca. 1.0, indicating that these copolymerization proceed in a random manner (or comonomer incorporations were random) [1–5,19].

Recently, *nonbridged* half-metallocene type group 4 transition metal complexes of the type,  $\text{Cp}'\text{M}(\text{L})\text{X}_2$  ( $\text{Cp}'$  = cyclopentadienyl group; M = Ti, Zr, Hf; L = anionic ligand such as OAr,  $\text{NR}_2$ ,  $\text{N}=\text{CR}_2$ ,  $\text{N}=\text{PR}_3$ , etc.; X = halogen, alkyl), become one of the promising candidates for new efficient catalysts for precise olefin polymerization [20–24]. This is



Scheme 2. Linked (amido)(cyclopentadienyl)titanium complex, constrained geometry catalyst (CGC) [13].

Table 1

Typical  $r_E$  and  $r_O$  values in ethylene/1-octene copolymerization using various group 4 transition metal catalysts<sup>a</sup>

Complexes	Temperature (°C)	$r_E$	$r_O$	$r_E \cdot r_O$
$Cp_2ZrCl_2^b$	40	32.8	0.05	1.17
$rac-Me_2Si(Ind)_2ZrCl_2^b$	40	18.9	0.014	0.27
$rac-Me_2Si(Benz[e]Ind)_2ZrCl_2^b$	40	10.7	0.076	0.81
$rac-Me_2Si(2-MeBenz[e]Ind)_2ZrCl_2^b$	40	10.1	0.118	1.2
$rac-Me_2Si(2-MeBenz[e]Ind)_2ZrCl_2^c$	40	8.16	0.14	1.14
$[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2^b$	40	4.1	0.29	1.19
$rac-Me_2Si(2-MeBenz[e]Ind)_2ZrCl_2^c$	0	4.71	0.22	1.06
$rac-Me_2Si(2-MeBenz[e]Ind)_2ZrCl_2^c$	20	6.45	0.18	1.14
$rac-Me_2Si(2-MeBenz[e]Ind)_2ZrCl_2^c$	40	8.16	0.14	1.14
$rac-Me_2Si(2-MeBenz[e]Ind)_2ZrCl_2^c$	60	10.61	0.1	1.11

<sup>a</sup> Conditions: in toluene,  $r_E \times r_O = 4[EE][OO]/[EO]^2$ ,  $r_E = k_{EE}/k_{EO} = [O]_0/[E]_0 \times 2[EE]/[EO + OE]$ ,  $r_O = k_{OO}/k_{OE} = [E]_0/[O]_0 \times 2[OO]/[EO + OE]$  ( $[E]_0$ ,  $[O]_0$ : initial monomer concentration).

<sup>b</sup> Cited from Ref. [15].

<sup>c</sup> Cited from Ref. [16].

because, as described below, that this type of complex catalyst has exhibited unique characteristics especially for ethylene (co)polymerizations affording new polymers that have never been prepared by conventional Ziegler–Natta catalysts, by ordinary metallocene type [1–4] and/or by so-called ‘constrained geometry’ (linked Cp-amide) type catalysts [4–5]. The other reasons are that the synthesis is not so complicated (relatively short synthetic steps with relatively high yield), and the ligand modification (sterically and/or electronically) should be easier especially than the ordinary bridged half-metallocene type complexes. Moreover, due to the efforts in early studies for organometallic chemistry of bis(amide) complexes of the type  $(R_2N)_2MX_2$  [25], or chelate bis(amide) complexes [26–27], many studies have been reported for design and synthesis of so called “*non-metallocene type*” transition metal complexes as catalysts for olefin polymerization [6]. In this article, group 4 half-metallocenes containing anionic ancillary donor ligands of type,  $Cp^*M(L)X_2$ , as new promising candidates as efficient catalysts for precise olefin polymerizations including our results have been reviewed.

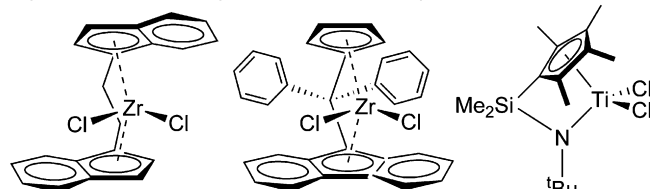
## 2. Nonbridged half-metallocenes

As described above, the linked (amide)(cyclopentadienyl) titanium complex of type,  $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$  (CGC), exhibits both high catalytic activities and efficient comonomer incorporations for ethylene/ $\alpha$ -olefin and ethylene/styrene copolymerizations [4–5,13]. The resultant copolymers possessed uniform comonomer distribution with relatively high molecular weights with unique microstructures (long chain branching etc.) [4–5]. In contrast, it has also been known that *nonbridged* half-titanocenes such as  $Cp^*Ti(OMe)_3$  ( $Cp^* = C_5Me_5$ ) exhibits remarkable catalytic activity for syndiospecific styrene polymerization (Scheme 3) [28]. Moreover,  $Cp^*TiMe_3$  was also known to exhibit catalytic activities for both ethylene polymerization and styrene polymerization in the presence of MAO or  $B(C_6F_5)_3$ , and the resultant polystyrene possessed both atactic (via cationic mechanism) and syndiotactic (via coordination insertion mechanism) stereo regularity and the ratios were dependent upon the polymerization temperature

[29–31]; this catalyst also polymerizes isobutene not via coordination insertion mechanism but via carbocationic mechanism (Scheme 4). No reports concerning efficient olefin polymerization catalysts with this type had thus been reported [32,33].

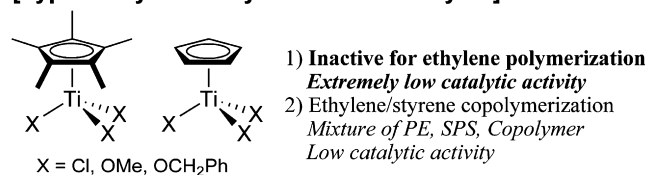
We reported in 1998 that the half-titanocenes containing an aryloxo ligand of the type,  $Cp^*TiCl_2(OAr)$  ( $Cp^*$  = cyclopentadienyl group;  $OAr$  = aryloxo group), exhibited not only notable catalytic activities for olefin polymerization [20,21,34], but also for efficient 1-butene incorporation in ethylene/1-butene copolymerization [21]. Later, we reported that these complexes also showed significant catalytic activities for syndiospecific styrene polymerization [35], whereas ordinary olefin polymerization catalysts such as metallocenes, linked half-titanocenes showed low (or negligible) catalytic activities for styrene polymerization, as shown in Scheme 3. Recently, half-metallocene type group 4 transition metal complexes containing anionic donor ligand of the type,  $Cp^*M(L)X_2$  ( $M = Ti, Zr, Hf$ ;  $L = OAr, NR_2, N=PR_3, N=CR_2$ , etc.;  $X =$  halogen, alkyl, etc., Scheme 5), became one of the promising candidates as the efficient catalysts [20–24], because this type of complex catalysts displayed unique characteristics as the catalysts producing

### [Typical Olefin Polymerization Catalysts]



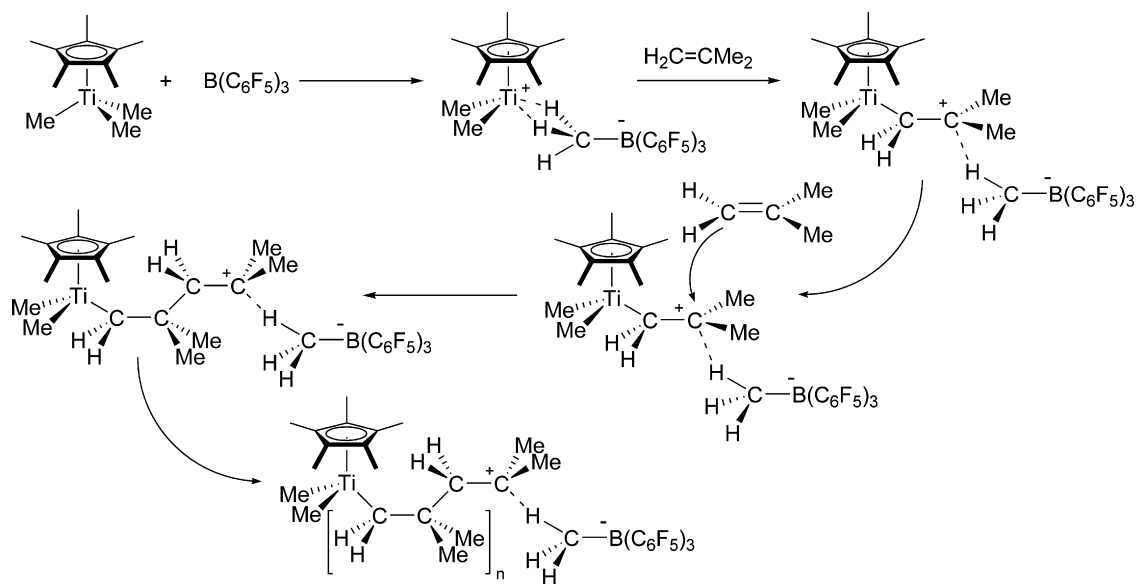
- 1) Inactive for styrene polymerization ... *Extremely low catalytic activity*
- 2) Ethylene/styrene copolymerization ... *Low styrene content, Low activity*

### [Typical Styrene Polymerization Catalysts]



- 1) Inactive for ethylene polymerization  
*Extremely low catalytic activity*
- 2) Ethylene/styrene copolymerization  
*Mixture of PE, SPS, Copolymer*  
*Low catalytic activity*

Scheme 3. Typical characteristics for olefin (styrene) polymerization catalysts.

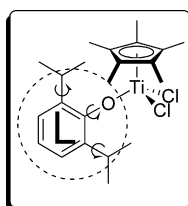


Scheme 4. Polymerization of isobutene initiated by  $\text{Cp}^*\text{TiMe}_2(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  reported by Baird [29].

new polymers that had never been prepared by conventional Ziegler–Natta catalysts, by ordinary metallocene type [1–4] and/or so-called ‘constrained geometry’ type catalysts [4–5].

We demonstrated that the half-titanocenes containing an aryloxo ligand of the type,  $\text{Cp}'\text{TiCl}_2(\text{OAr})$  ( $\text{OAr}$  = aryloxo group), displayed the unique characteristics especially for copolymerization of ethylene with  $\alpha$ -olefin [36], styrene [35a,37], norbornene [38], and revealed that an efficient catalyst for desired polymerization can be simply modified by replacement of the cyclopentadienyl fragment,  $\text{Cp}'$ . More recently, we had shown that efficient copolymerizations of ethylene with cyclohexene (CHE) [39], 2-methyl-1-pentene (2M1P) [40], and with vinylcyclohexane [41] had been achieved as the first examples by using these complex catalysts. Moreover, these catalysts showed favored repeated 1,2-insertion in polymerization of 1,5-hexadiene, affording polymers containing olefins in the side chain with uniform distribution [42].

Selected examples for *nonbridged* half-metallocenes containing anionic donor ligands,  $\text{Cp}'\text{M}(\text{L})\text{X}_2$ , are summarized in Schemes 6 [20,21,35,37,38,43–64] and Scheme 7 [65–80]. Many examples were known for synthesis of this type of complexes and for use as olefin polymerization catalysts, especially for ethylene polymerization. Some examples were known to exhibit remarkable activities for ethylene polymerization, or isospecific living polymerization of  $\alpha$ -olefins, as described below.



**Basic Concept: Catalyst Design**

1) *Nonbridged complexes*

$\text{Cp}'\text{M}(\text{L})\text{X}_2$

*L* = Anionic ancillary donor ligand  
Easy to prepare various  $\text{Cp}'$  & *L* derivatives

2) *High catalytic activity*

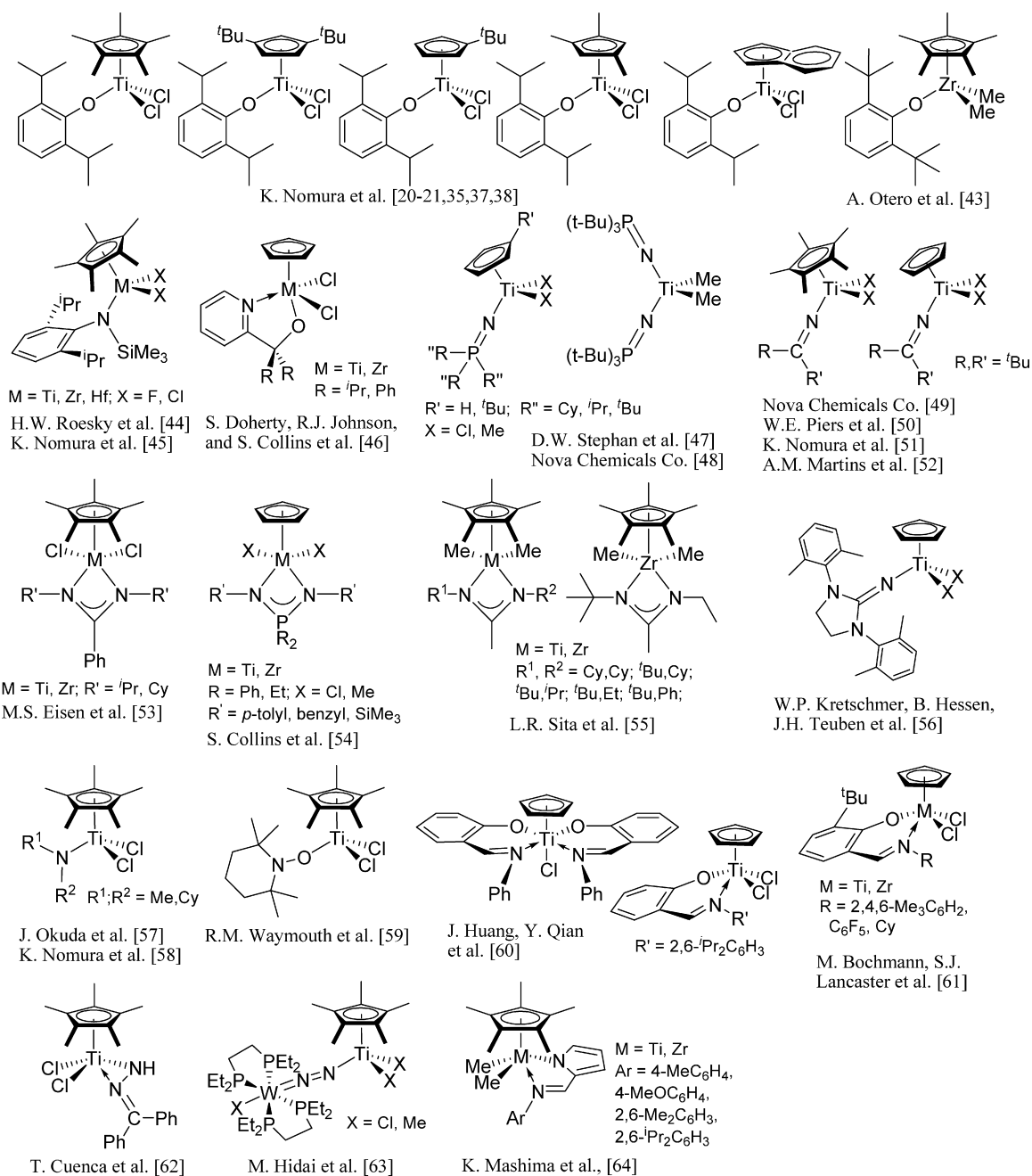
3) *Control of monomer reactivity*

Scheme 5. Design for *nonbridged* half-titanocenes containing anionic donor ligands as the precise olefin polymerization catalysts.

### 2.1. Olefin polymerization by half-titanocenes containing aryloxo ligands

It has been known that the ligand modification is very important in order for metal catalyzed olefin polymerization to proceed with remarkable catalytic activities. For example, as shown in Scheme 8, both substituents on cyclopentadienyl and aryloxo groups affected the catalytic activity for ethylene polymerization [20,21].  $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  (**1a**) exhibited notable activities, and the activity by  $\text{Cp}'\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  increased in the order:  $\text{Cp}' = \text{Cp}^* \gg 1,3\text{-}i\text{Bu}_2\text{C}_5\text{H}_3 > 1,3\text{-Me}_2\text{C}_5\text{H}_3, {}^t\text{BuC}_5\text{H}_4 \gg \text{Cp}$ . This seems the similar observation for syndiospecific styrene polymerization using a series of  $\text{Cp}'\text{Ti}(\text{OMe})_3$  complexes [28c–e], and the similar explanation that the stabilization of the active site by more electron-donating substituents is important for the high activity can be thus assumed. On the other hand, as also shown in Scheme 8, the steric bulk of phenoxy ligand containing substituents in the 2,6-position should be very important for exhibiting the high activity. We assumed that the steric bulk of aryloxo ligand stabilized the catalytically active species under the polymerization conditions in the presence of cocatalyst (to protect the probable accompanied reaction with Al alkyls, dissociation of the aryloxo) [20,21].

In order to explore the reason why both  $\text{Cp}^*$  and 2,6-diisopropylphenoxy ligand in **1a** are prerequisite for the remarkable activity in ethylene polymerization, we prepared various  $\text{Cp}$  and aryloxo analogues and determined the structures by X-ray crystallography [20,21,81]. As shown in Table 2, the bond angle ( $173.0^\circ$ ) of  $\text{Ti}-\text{O}-\text{C}$  (phenoxy) for  $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  (**1a**), which was the most effective catalyst precursor, is significantly different from those for the other  $\text{Cp}$  derivatives,  $\text{Cp}'\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  ( $\text{Cp}' = \text{Cp}, 1,3\text{-}i\text{Bu}_2\text{C}_5\text{H}_3, 163.0\text{--}163.1^\circ$ ), we thus assumed that both  $\text{Cp}^*$  and the diisopropyl group sterically force the more open  $\text{Ti}-\text{O}-\text{C}$  bond angle, which leads to more  $\text{O} \rightarrow \text{Ti} \pi$  donation into Ti; this

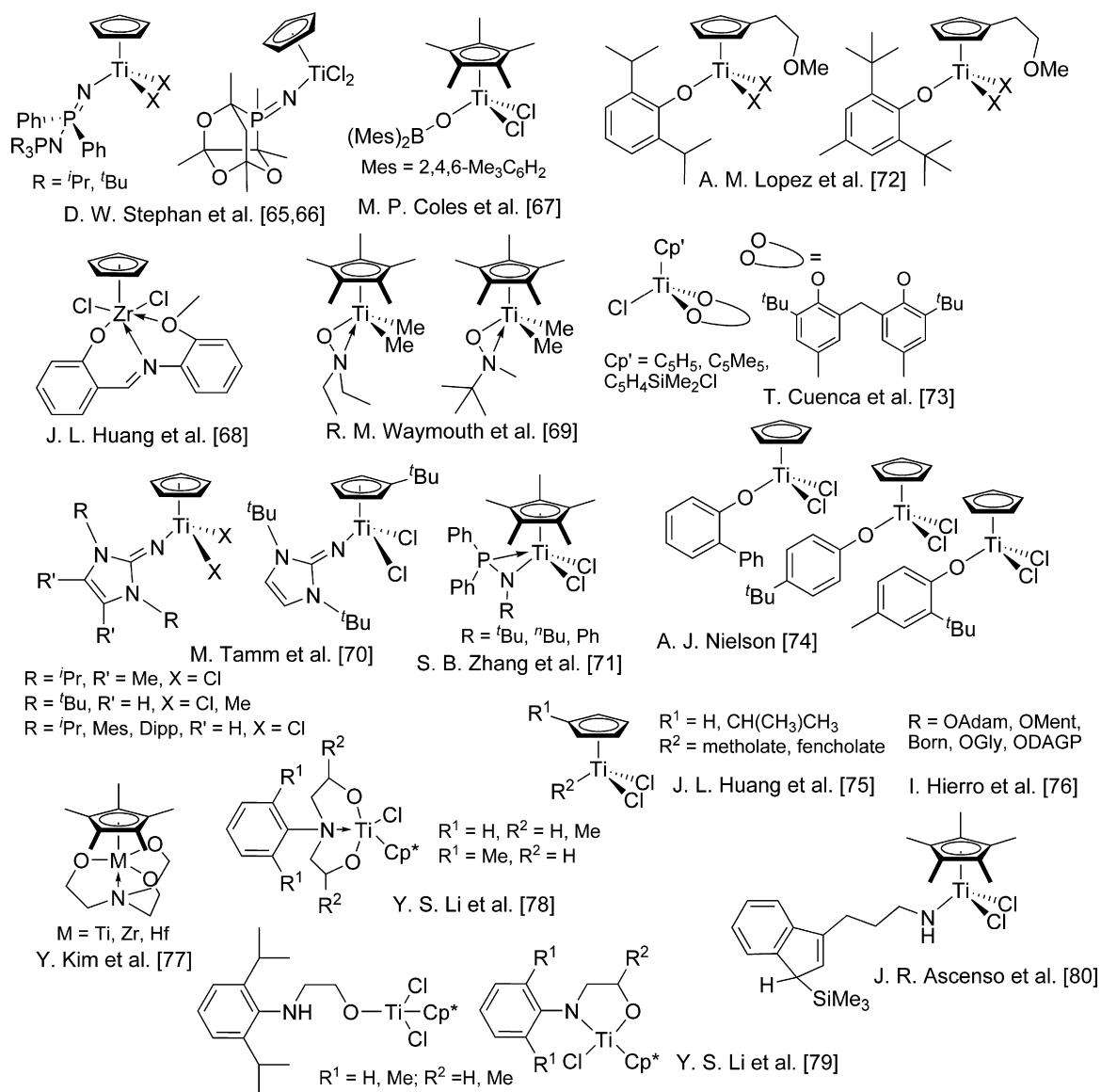


Scheme 6. Selected examples for nonbridged half-metallocene type group 4 complexes as olefin polymerization catalysts.

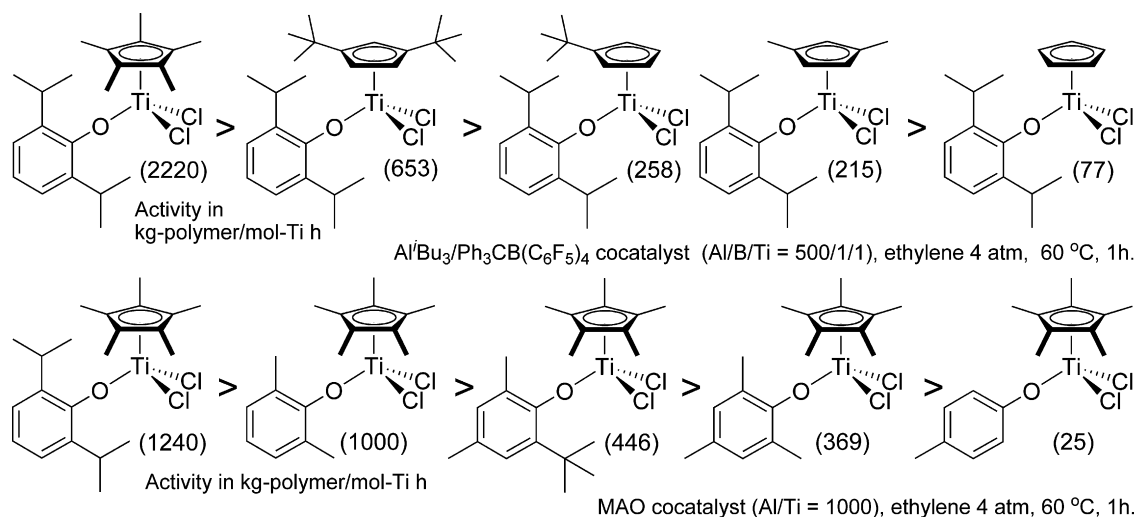
along with the more electron donating Cp\* (as compared with Cp, *t*-BuCp, Me<sub>2</sub>Cp) stabilizes the active species, leading to the higher activity [20,21].

Table 3 summarizes selected results for bond distances and angles in the various Cp\*-aryloxy analogues, Cp\*TiCl<sub>2</sub>(OAr) [81–84]. It should be noted that the bond angles of Ti–O–C (phenyl) the 2,6-diisopropylphenoxy analogues, (173.0, 174.6° for Ar = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,6-*i*-Pr<sub>2</sub>-4-*t*-BuC<sub>6</sub>H<sub>2</sub>, respectively) were larger than those in the other Cp\* derivatives (155.5–162.3°) except Cp\*TiCl<sub>2</sub>(O-2,6-Ph<sub>2</sub>-3,5-*t*-Bu<sub>2</sub>C<sub>6</sub>H) (176.9°) [84]. Although we assumed above [20,21] that both Cp\* and diisopropyl group ‘sterically’ force the more open Ti–O–C bond angle, the bond angle for the di-*tert*-butyl ana-

logue was small (155.5°). The similar large bond angle was observed in Cp\*TiCl<sub>2</sub>(O-2,6-Ph<sub>2</sub>-3,5-*t*-Bu<sub>2</sub>C<sub>6</sub>H) whereas the value in Cp\*TiCl<sub>2</sub>(O-2,6-Ph<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) was rather small (160.6°). These results might suggest that the unique bond angles in Ti–O–C (phenyl) were affected by substituents in both cyclopentadienyl and aryloxy ligands. 1-Hexene polymerization catalyzed by various Cp\*TiCl<sub>2</sub>(OAr)–MAO catalyst systems were explored and the phenoxide complexes possessing *t*-Pr group in 2,6-position exhibited exceptionally high catalytic activities as assumed from the above results (Table 4). The results suggest that the unique bond angles in Ti–O–C (phenyl) affect the high catalytic activity



Scheme 7. More recent examples for nonbridged half-metallocene type group 4 complexes as olefin polymerization catalysts.



Scheme 8. Effect of substituents on cyclopentadienyl and aryloxy ligands in ethylene polymerization (ethylene 4 atm, 60 °C, 1 h) [20,21].

Table 2  
Selected bond distances and angles for Cp<sup>\*</sup>TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [21]

Compound	Cp'	Cp	1,3- <i>i</i> -Bu <sub>2</sub> C <sub>5</sub> H <sub>3</sub>	Cp <sup>*</sup>
Bond distances (Å)				
Ti(1)—Cl(1)		2.262(1)	2.2553(8)	2.305(2)
Ti(1)—C(1) in Cp		2.282(8)	2.379(3)	2.367(7)
Ti(1)—C(2) in Cp		2.299(5)	2.378(3)	2.345(7)
Ti(1)—C(3) in Cp		2.325(5)	2.410(2)	2.368(7)
Ti(1)—O(1)		1.760(4)	1.773(3)	1.772(3)
Bond angles (°)				
Cl(1)—Ti—Cl(2)		104.23(7)	103.46(3)	103.45(5)
Cl(1)—Ti—O(1)		102.53(9)	103.62(6)	99.1(2)
Cl(2)—Ti—O(1)		102.53(9)	98.57(6)	104.1(2)
Ti—O—C(6) in phenyl		163.0(4)	163.1(2)	173.0(3)

by more O → Ti π donation into the titanium, leading to stabilize the catalytically active species for exhibiting the higher catalytic activity.

Since the unique bond angle in Ti—O—C (phenyl) seems to be originated from the ligand set (Cp<sup>\*</sup> and 2,6-diisopropylphenoxy), we prepared and determined the structures Cp<sup>\*</sup>Ti(X)(Y)(O-2,6-*i*-Pr<sub>2</sub>-4-R'<sup>1</sup>-4-R'<sup>2</sup>C<sub>6</sub>H<sub>2</sub>) (X, Y = Cl, Cl, Me, Me, Me, CF<sub>3</sub>SO<sub>3</sub>, R' = H or *t*Bu) by X-ray crystallography [81,85]. The selected bond angles and distances are summarized in Table 5 and structures for Cp<sup>\*</sup>TiMe<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and Cp<sup>\*</sup>TiMe(CF<sub>3</sub>SO<sub>3</sub>)(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) are shown in Fig. 1 [85]. Although no significant differences in the bond distances were observed among these complexes, the bond angles in X—Ti—Y were influenced by the anionic ligands (X, Y), probably due to the increased steric bulk of Me, CF<sub>3</sub>SO<sub>3</sub> ligands compared to Cl. It should be noted that the bond angles in Ti—O—C (phenyl) were somewhat large in all cases (166.2–174.6°), clearly suggesting that both Cp<sup>\*</sup> and the 2,6-diisopropyl-substituted aryloxo ligand form the unique bond angle, leading to more O → Ti π donation into the titanium.

The observed catalytic activity was extremely low if B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was used as the cocatalyst for 1-hexene polymerization in the presence of Cp<sup>\*</sup>TiMe<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**1b**)—Al<sup>*i*</sup>Bu<sub>3</sub>

Table 4  
1-Hexene polymerization by Cp<sup>\*</sup>TiCl<sub>2</sub>(O-2,6-R<sup>1</sup>-2-4-R<sup>2</sup>C<sub>6</sub>H<sub>2</sub>)—MAO catalyst systems [81]<sup>a</sup>

R <sup>1</sup> , R <sup>2</sup>	Yield (mg)	Activity <sup>b</sup>	M <sub>n</sub> <sup>c</sup> (×10 <sup>-4</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>
Me, H	40	240	14.2	1.66
Me, Me	58	348	13.2	1.66
<i>i</i> Pr, H	445	2670	46.1	1.42
<i>i</i> Pr, <i>t</i> Bu	448	2690	26.1	1.8
<i>t</i> Bu, H	26	156	23.7	1.93
<i>t</i> Bu, Me	36	216	28.4	1.63

<sup>a</sup> Polymerization conditions: 1-hexene 10 mL, *n*-hexane 10 mL, catalyst 0.5 μmol (complex 2.0 μmol/mL toluene), MAO (prepared by removing toluene and AlMe<sub>3</sub>) 3.0 mmol, 25 °C, 20 min.

<sup>b</sup> Activity in kg polymer/mol Ti h.

<sup>c</sup> GPC data in THF vs. polystyrene standards.

catalyst system, although the significant catalytic activity was observed if [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was used in place of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> [85]. The polymerization took place in a quasi living manner with remarkably high catalyst efficiency even at -30 °C, when both [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and Al<sup>*i*</sup>Bu<sub>3</sub> were used as cocatalysts under the optimized conditions. The resultant poly(1-hexene) possessed high molecular weight with narrow molecular weight distribution (M<sub>n</sub> = 1.87 × 10<sup>6</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.27) [86]. The reaction of **1b** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in toluene-*d*<sub>8</sub> afforded decomposed compound, Cp<sup>\*</sup>Ti(C<sub>6</sub>F<sub>5</sub>)[CH<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>](O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), (and/or intermediates) even at -70 °C, whereas no decomposition was observed if the reaction of **1b** was employed with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] [85]. The species generated from the reaction consumed 1-hexene exclusively even at -30 °C, suggesting that the generated cationic Ti(IV) species play a role in this catalysis. These results well explained the effect of borate cocatalysts in the 1-hexene polymerization.

Rothwell et al. also prepared CpTiMe<sub>2</sub>(OAr) complex containing *ortho*-naphthylphenoxide ligand [84], and addition of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in benzene gave thermally unstable cationic complex, CpTiMe[(μ-Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>](OAr) (**2**), which then gradually decomposed at ambient temperature to afford the neutral species,

Table 3  
Selected bond distances and angles for Cp<sup>\*</sup>TiCl<sub>2</sub>(O-2,6-R<sub>2</sub>-4-R'<sup>1</sup>-4-R'<sup>2</sup>C<sub>6</sub>H<sub>2</sub>) [81]

R, R'	Me, H <sup>a</sup>	Me, Me <sup>b</sup>	<i>i</i> Pr, H <sup>c</sup>	<i>i</i> Pr, <i>t</i> Bu <sup>d</sup>	<i>t</i> Bu, H <sup>b</sup>	Ph, H <sup>d</sup>	Ph, 3,5- <i>t</i> Bu <sub>2</sub> <sup>e</sup>
Bond distances (Å)							
Ti(1)—Cl(1)	2.273(6)	2.262(2)	2.305(2)	2.268(1)	2.2674(10)	2.2693(13)	2.258(1)
Ti(1)—C(1) in Cp	2.329(3)	2.344(6)	2.367(7)	2.345(4)	2.359(4)	2.355(4)	2.340(3)
Ti(1)—C(2) in Cp	2.341(2)	2.389(7)	2.345(7)	2.417(4)	2.375(3)	2.348(4)	2.369(3)
Ti(1)—C(3) in Cp	2.398(2)	2.374(7)	2.368(7)	2.399(4)	2.370(3)	2.377(4)	2.420(3)
Ti(1)—O(1)	1.785(2)	1.781(4)	1.772(3)	1.779(3)	1.804(2)	1.811(3)	1.804(2)
Bond angles (°)							
Cl(1)—Ti—Cl(2)	103.3(2)	103.2(1)	103.45(5)	103.68(5)	98.10(4)	98.70(5)	100.44(4)
Cl(1)—Ti—O(1)	101.7(1)	102.0(1)	99.1(2)	102.73(10)	103.22(6)	104.33(10)	103.68(7)
Cl(2)—Ti—O(1)	101.7(1)	101.6(1)	104.1(2)	101.83(10)	103.22(6)	105.20(10)	104.34(7)
Ti—O—C(6) in phenyl	162.3(2)	162.1(4)	173.0(3)	174.6(3)	155.5(2)	160.6(3)	176.90(19)

<sup>a</sup> Cited from Ref. [82].

<sup>b</sup> Cited from Ref. [81].

<sup>c</sup> Cited from Ref. [21].

<sup>d</sup> Cited from Ref. [83].

<sup>e</sup> Cited from Ref. [84].

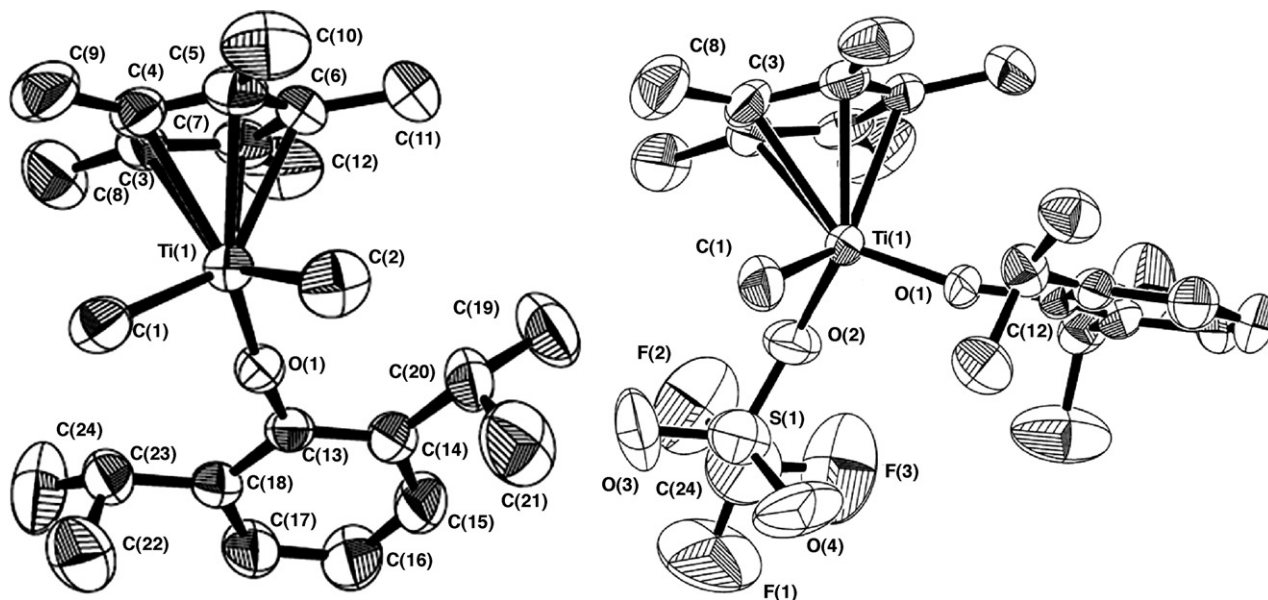


Fig. 1. Structures for  $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  (left) and  $\text{Cp}^*\text{TiMe}(\text{CF}_3\text{SO}_3)(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  (right) [85].

Table 5  
Selected bond distances and angles for  $\text{Cp}^*\text{Ti}(\text{X})(\text{Y})(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  [81]

Compound/R' X, Y	H <sup>a</sup> Cl, Cl	H <sup>b</sup> Me, Me	H <sup>b</sup> Me, CF <sub>3</sub> SO <sub>3</sub>
<b>Bond angles (°)</b>			
Ti(1)—Cl(1) or C in Me	2.305(2)	2.101(3)	2.093(8)
Ti(1)—C(1) in Cp	2.367(7)	2.338(3)	2.346(6)
Ti(1)—C(2) in Cp	2.345(7)	2.350(2)	2.377(6)
Ti(1)—C(3) in Cp	2.368(7)	2.374(2)	2.353(6)
Ti(1)—O(1)	1.772(3)	1.790(2)	1.778(4)
<b>Bond distances (Å)</b>			
X—Ti—Y	103.45(5)	99.8(1) <sup>c</sup>	97.4(3) <sup>d</sup>
X—Ti—O(1), X = Cl or C in Me	99.1(2)	101.9(1) <sup>e</sup>	102.1(2) <sup>e</sup>
Y—Ti—O(1)	104.1(2)	102.9(1)	106.6(2)
Ti—O—C in phenyl	173.0(3)	168.7(1)	166.2(4)

<sup>a</sup>  $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  cited from Refs. [20,21].

<sup>b</sup>  $\text{Cp}^*\text{TiMe}(\text{Y})(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  (Y = Me, CF<sub>3</sub>SO<sub>3</sub>) cited from Ref. [85].

<sup>c</sup> Me—Ti—Me bond angle.

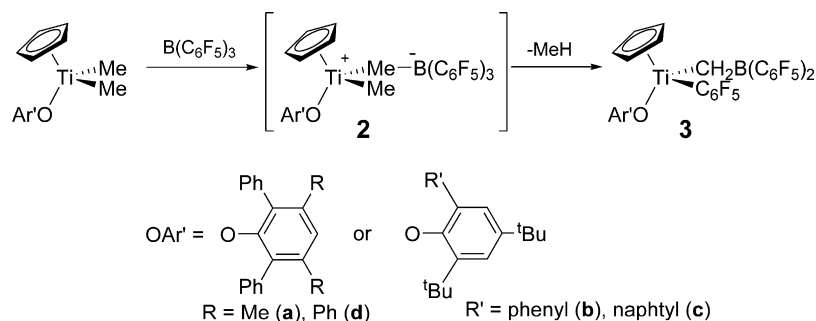
<sup>d</sup> Me—Ti—O in CF<sub>3</sub>SO<sub>3</sub> bond angle.

<sup>e</sup> O(1)—Ti—C in Me bond angle.

$\text{CpTi}(\text{C}_6\text{F}_5)[\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2](\text{OAr})$  (**3**), followed by methane elimination (Scheme 9) [84].

## 2.2. Olefin polymerization by half-titanocenes containing various anionic ancillary donor ligands

Roesky et al. reported the synthesis of both Cp'-amide complexes of the type,  $\text{Cp}^*\text{MX}_2[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)]$  (M = Zr, Hf; X = F, Cl) and bis(amide) complexes of the type,  $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)\text{N}]_2\text{MX}_2$  in 1996 [44]. They attempted ethylene polymerization in the presence of MAO, and found that the half-metallocene analogue would be more suited than the bis(anilide) analogues as the polymerization catalysts (Table 6). In addition, Zr complexes exhibited higher catalytic activities than the related Hf complexes, but the significant differences could not be observed between chlorides and fluorides, although they expected the improvement of the activity with fluoride as they could observe in the syndiospecific styrene polymerization with  $\text{Cp}'\text{TiX}_3\text{-MAO}$  catalysts [28g]. No data concerning molecular weights and molecular weight distributions for the resultant polyethylene were given.



Scheme 9. Reaction of  $\text{Cp}'\text{TiMe}_2(\text{OAr})$  with  $\text{B}(\text{C}_6\text{F}_5)_3$  [84].



Table 6  
Ethylene polymerization with  $\text{Cp}^* \text{MX}_2[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)]$ ,  $\text{MX}_2[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)]_2$ –MAO catalyst systems [44]<sup>a</sup>

Complex	Al/M <sup>b</sup>	Activity <sup>c</sup>
$\text{Cp}^* \text{ZrCl}_2[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)]$	3000	476
$\text{Cp}^* \text{HfF}_2[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)]$	1000	6
$\text{Cp}^* \text{ZrF}_2[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)]$	3000	293
$\text{Cp}^* \text{HfF}_2[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)]$	1000	2
$\text{ZrCl}_2[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)]_2$	1000	13
$\text{HfCl}_2[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)]_2$	1000	Trace
$\text{ZrF}_2[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)]_2$	1000	9
$\text{HfF}_2[\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)]_2$	1000	Trace

<sup>a</sup> Reaction conditions: toluene 100 mL, ethylene 1 atm, 30 min, 250 mL scale autoclave.

<sup>b</sup> Molar ratio of Al/M.

<sup>c</sup> Activity in kg polymer/mol M h.

The observed catalytic activities for ethylene polymerizations with a series of  $\text{Cp}'\text{TiCl}_2[\text{N}(2,6\text{-}\text{Me}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)]$  complexes at 25 °C increased in the order:  $\text{Cp}' = \text{Cp}^*$  (902 kg PE/mol Ti h) > 1,3- $\text{Me}_2\text{C}_5\text{H}_3$  (104), Cp (113) (Table 7) [45]. These results suggest that the introduction of electron-donating group increases the activity. The activity by the

Cp-Si<sup>i</sup>BuMe<sub>2</sub> analogue seemed somewhat higher than the Cp-SiMe<sub>3</sub> analogue under the same conditions, and this trend is similar to that observed for ethylene (co)polymerization with a series of  $[1,8\text{-C}_{10}\text{H}_6(\text{NR})_2]\text{TiCl}_2$  [R = SiMe<sub>3</sub>, Si<sup>i</sup>BuMe<sub>2</sub>, Si<sup>i</sup>Pr<sub>3</sub>]–MAO catalyst systems [26s,t,87]. The observed effect in the anilide ligand for the activity would be thus explained by an assumption that the stability of catalytically active species, especially the stability of the *N*-alkylsilyl bond in the solution under these reaction conditions, affected the catalytic activity [45].

$\text{Cp}^* \text{TiCl}_2(\text{NMe}_2)$  exhibited moderate catalytic activity in the presence of MAO (Table 8) [57], and the activity slightly decreased if the ordinary MAO was used in place of MAO prepared by removing AlMe<sub>3</sub>. The activity further decreased significantly at 50 °C, and the decrease would be due to the dissociation of amide ligand from the metal center by reaction with AlMe<sub>3</sub>. In contrast,  $\text{Cp}^* \text{TiCl}_2[\text{N}(\text{Me})\text{Cy}]$  exhibited notable catalytic activity for ethylene polymerization [58], and the activity apparently increased at lower concentration conditions. The Me<sub>2</sub>Cp analogues also showed relatively high catalytic activity for ethylene polymerization. The observed results in  $\text{Cp}^* \text{TiCl}_2[\text{N}(\text{Me})\text{Cy}]$  suggest that the activity can be

Table 7  
Ethylene polymerization by  $\text{Cp}'\text{TiCl}_2[\text{N}(2,6\text{-}\text{Me}_2\text{C}_6\text{H}_3)(\text{R})]$ –MAO catalyst systems (R = SiMe<sub>3</sub>, Cp' = Cp\*, 1,3-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>, Cp; R = Si<sup>i</sup>BuMe<sub>2</sub>, Cp' = Cp) [44]<sup>a</sup>

Catalyst Cp', R (μmol)	Al/Ti <sup>b</sup>	Temperature (°C)	Yield <sup>c</sup> (mg)	Activity <sup>d</sup>	$M_w^e$ ( $\times 10^{-4}$ )	$M_w/M_n^e$
$\text{Cp}^*$ , SiMe <sub>3</sub> (1.0)	3000	25	435	870	Insoluble <sup>f</sup>	
$\text{Cp}^*$ , SiMe <sub>3</sub> (1.0)	5000	25	451	902	Insoluble <sup>f</sup>	
Me <sub>2</sub> Cp, SiMe <sub>3</sub> (10.0)	500	25	518	104	0.19	2.00
Me <sub>2</sub> Cp, SiMe <sub>3</sub> (10.0)	500	40	140	28	0.18	2.01 <sup>g</sup>
Cp, SiMe <sub>3</sub> (10.0)	500	25	567 (373)	113	34.2 <sup>h</sup>	198
Cp, Si <sup>i</sup> BuMe <sub>2</sub> (10.0)	500	25	684 (477)	137		
Cp, Si <sup>i</sup> BuMe <sub>2</sub> (10.0)	500	40	257 (183)	51	28.4 <sup>i</sup>	96.1

<sup>a</sup> Polymerization conditions: toluene 30 mL, MAO (prepared by removing toluene and AlMe<sub>3</sub>), ethylene 6 atm, 30 min.

<sup>b</sup> Molar ratio of Al/Ti.

<sup>c</sup> In parentheses, the yield of low molecular weight oligomer oil (soluble in acidified ethanol and extracted with chloroform).

<sup>d</sup> Activity = kg PE/mol Ti h.

<sup>e</sup> GPC data (acidified ethanol insoluble portion) in *o*-dichlorobenzene vs. polystyrene standard.

<sup>f</sup> Resultant PE was insoluble in hot *o*-dichlorobenzene.

<sup>g</sup> High molecular weight PE was also observed in a trace amount.

<sup>h</sup> Mixture of high and low molecular weight polymers.

<sup>i</sup> Bimodal molecular weight distribution consisted of  $M_w = 5.01 \times 10^5$ ,  $2.19 \times 10^3$ .

Table 8  
Ligand effect in ethylene polymerization by  $\text{Cp}'\text{TiCl}_2[\text{NR}^1\text{R}^2]$  [Cp' = Cp\* and R<sup>1</sup>, R<sup>2</sup> = Me, Me, Me, Et, Me, Cy (Cy = cyclohexyl); Cp' = 1,3-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub> and R<sup>1</sup>, R<sup>2</sup> = Me, Cy, Cy, Cy]–MAO catalyst systems [58]<sup>a</sup>

Catalyst (μmol) Cp'; R <sup>1</sup> , R <sup>2</sup>	Al cocatalyst	Al/Ti <sup>b</sup>	Temperature (°C)	Activity (kg PE/mol Ti h)
$\text{Cp}^*$ ; Me, Me (2.0)	MAO	1500	25	1600
$\text{Cp}^*$ ; Me, Me (2.0)	MAO <sup>c</sup>	1500	25	1430
$\text{Cp}^*$ ; Me, Me (2.0)	MAO <sup>c</sup>	1500	50	180
$\text{Cp}^*$ ; Me, Et (2.0)	MAO	1500	25	1680
$\text{Cp}^*$ ; Me, Cy (1.0)	MAO	3000	25	3980 <sup>d</sup>
$\text{Cp}^*$ ; Me, Cy (0.5)	MAO	6000	25	4540
1,3-Me <sub>2</sub> Cp; Me, Cy (1.0)	MAO	3000	25	1520
1,3-Me <sub>2</sub> Cp; Cy, Cy (1.0)	MAO	3000	25	2000

<sup>a</sup> Polymerization conditions: toluene 30 mL, MAO (prepared by removing toluene and AlMe<sub>3</sub>) 3.0 mmol (Al), ethylene 6 atm, 10 min.

<sup>b</sup> Molar ratio of Al/Ti.

<sup>c</sup> Commercially available MAO (contains AlMe<sub>3</sub>) was used.

<sup>d</sup> GPC data in *o*-dichlorobenzene vs polystyrene standards:  $M_w = 1.65 \times 10^4$ ,  $M_w/M_n = 2.88$  and  $M_w = 6.79 \times 10^5$ ,  $M_w/M_n = 1.99$  (small amount).

Table 9  
Ethylene polymerization with CpMCl<sub>2</sub>[OCR<sub>2</sub>-(2-C<sub>5</sub>H<sub>4</sub>N)]-MAO catalyst systems [46]<sup>a</sup>

Complex M; R	Activity <sup>b</sup>	<i>M<sub>w</sub></i> <sup>c</sup> (×10 <sup>-4</sup> )	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>c</sup>
Ti; <sup><i>i</i></sup> Pr	80	45.0	2.00
Ti; Ph	320	54.4	1.86
Zr; <sup><i>i</i></sup> Pr	430	56.7	2.17
Zr; <sup><i>i</i></sup> Pr	710	86.2	3.44
Zr; Ph	370	65.8	1.74

<sup>a</sup> Reaction conditions: toluene 450 mL, ethylene 75 psig (5.1 atm), 30 °C, MAO (Al/M = 1000, molar ratio), 1000 mL scale autoclave.

<sup>b</sup> Activity in kg polymer/mol M h.

<sup>c</sup> GPC data in 1,2,4-trichlorobenzene vs. polyethylene standard.

tuned only by replacing of one methyl group on the amide ligand into cyclohexyl group. An assumption that introduction of electron-donating substituents into the amide group increases the activity can be thus considered, because the observed activity was higher than that reported by Cp<sup>\*</sup>TiCl<sub>2</sub>[N(SiMe<sub>3</sub>)(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)] under the same conditions (1080 kg PE/mol Ti h) [45]. The effect of increased steric bulk with cyclohexyl group would also be considered, because the dissociation of amide ligand by Al alkyls would be disturbed by the steric bulk of cyclohexyl fragment.

Polymerization of ethylene by cyclopentadienyl-pyridylalkoxide complex of type, CpMCl<sub>2</sub>[OCR<sub>2</sub>(2-NC<sub>5</sub>H<sub>4</sub>)], was reported by Doherty and Errington [46]. The results are summarized in Table 9. Stable polymerization profiles with little evidence for catalyst decay were observed under these conditions, and the nature of R group affected the catalytic activity. The activities observed here were relatively higher than that reported by Chien and Rausch with [(C<sub>5</sub>Me<sub>4</sub>)(CH<sub>2</sub>)<sub>2</sub>(NMe<sub>2</sub>)]TiCl<sub>3</sub> complex-MAO catalyst system [28h,i], and a steric effect and/or greater π-donation to the metal center by the oxygen atom in the more electron-rich alkoxide complexes was thus assumed for the improved catalytic activity.

Eisen et al. prepared bis(benzamidinato) titanium and zirconium complexes of the type, [PhC(NR)<sub>2</sub>]<sub>2</sub>MCl<sub>2</sub> (M = Ti, Zr; R = <sup>*i*</sup>Pr, Cy), and [PhC(N<sup>*i*</sup>Pr)<sub>2</sub>]<sub>2</sub>ZrCl<sub>2</sub> showed moderate activity for ethylene polymerization in the presence of MAO [53]. Although they also prepared [PhC(NR)<sub>2</sub>]<sub>2</sub>Cp<sup>\*</sup>MCl<sub>2</sub> (M = Ti, Zr; R = <sup>*i*</sup>Pr, Cy), but these complexes showed the lower activities

[53]. Sita et al. prepared various half-titanocenes containing acetamidinato ligand of the type, Cp<sup>*i*</sup>TiMe<sub>2</sub>[NR<sup>1</sup>C(Me)NR<sup>2</sup>] (R<sup>1</sup>, R<sup>2</sup> = Cy, Cy, <sup>*t*</sup>Bu, 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, <sup>*t*</sup>Bu, Et, <sup>*i*</sup>Bu, <sup>*i*</sup>Pr, <sup>*t*</sup>Bu, Cy), and examined the ethylene polymerization in the presence of MAO [55b]. The observed activity by Cp<sup>\*</sup>TiMe<sub>2</sub>[NCyC(Me)NCy] was low [22 kg PE/mol Ti h, 25 °C, 1 atm of ethylene, in toluene, Al/Ti = 80–90], and the activity with Cp<sup>\*</sup>TiMe<sub>2</sub>[N<sup>*t*</sup>BuC(Me)N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)] was extremely low (0.1 kg PE/mol Ti h) [55b].

Zirconium complexes containing iminophosphonamide ligand of type, [R<sub>2</sub>P(NR')<sub>2</sub>]<sub>2</sub>MCl<sub>2</sub> and CpZrCl<sub>2</sub>[RP(NR')<sub>2</sub>], were prepared by Collins et al. [54], and [Ph<sub>2</sub>P{N(4-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>}]<sub>2</sub>ZrCl<sub>2</sub> and CpZrCl<sub>2</sub>[Et<sub>2</sub>P(NSiMe<sub>3</sub>)<sub>2</sub>] exhibited high catalytic activity for ethylene polymerization even at relatively high temperature (Table 10). On the other hand, bis(iminophosphonamido)titanium(IV) complexes were about 50–100 time less active under these conditions. Although the dimethyl complex was inactive for ethylene polymerization in the presence of MAO under the same conditions, notable increase in the activity was observed by the addition of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (5.30 × 10<sup>3</sup> kg PE/mol Zr h).

Stephan et al. focused on using sterically bulky phosphinimide ligand as the steric equivalent to cyclopentadienyl group [47], because the bulky ligand would provide environment sterically/electronically similar to cyclopentadienyl fragment as previously noted by Dehnicke et al. [88]. They prepared series of cyclopentadienyl-phosphinimide titanium(IV) complexes of type, Cp<sup>*i*</sup>Ti(NPR<sub>3</sub>)X<sub>2</sub>, and explored effect of the substituents on both Cp<sup>*i*</sup> and NPR<sub>3</sub> groups for the catalytic activity in ethylene polymerization (Table 11) [47a,d]. These complexes exhibited remarkable activities for ethylene polymerization in the presence of MAO, and the activity improved with the combination of borate compound, [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Substituents on both Cp<sup>*i*</sup> and phosphinimide ligands play an essential role for exhibiting the high activity, and use of N=PCy<sub>3</sub> ligand was effective. The *tert*-BuCp analogues were more suited than the Cp analogues, suggesting that electron-donating substituents on Cp<sup>*i*</sup> increase the catalytic activity. Analogous zirconium complexes were also prepared, but these complexes showed low catalytic activities for ethylene polymerization in the presence of MAO [47c]. The activities by the zirconium analogues improved upon the presence of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] cocatalyst [47e].

Table 10  
Ethylene polymerization with Cp<sup>\*</sup>MCl<sub>2</sub>[R<sup>1</sup><sub>2</sub>P(NR<sup>2</sup>)<sub>2</sub>], [R<sup>1</sup><sub>2</sub>P(NR<sup>2</sup>)<sub>2</sub>]<sub>2</sub>MCl<sub>2</sub>, (M = Ti, Zr)-MAO catalyst systems [54]<sup>a</sup>

Complex	Temperature (°C)	Activity <sup>b</sup> (×10 <sup>-3</sup> )	<i>M<sub>n</sub></i> <sup>c</sup> (×10 <sup>-4</sup> )	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>c</sup>
CpZrCl <sub>2</sub> [Et <sub>2</sub> P{N(SiMe <sub>3</sub> ) <sub>2</sub> }]	50	660		
CpZrCl <sub>2</sub> [Et <sub>2</sub> P{N(SiMe <sub>3</sub> ) <sub>2</sub> }]	70	8900	9.3	2.45
[Ph <sub>2</sub> P{N( <i>p</i> -tolyl) <sub>2</sub> }] <sub>2</sub> ZrCl <sub>2</sub>	50	7900	14.4	2.07
[Ph <sub>2</sub> P{N( <i>p</i> -tolyl) <sub>2</sub> }] <sub>2</sub> ZrCl <sub>2</sub>	70	2500	7.9	3.55
[Ph <sub>2</sub> P{N( <i>p</i> -tolyl) <sub>2</sub> }] <sub>2</sub> TiMe <sub>2</sub>	50	55	3.5	1.67
[Ph <sub>2</sub> P{N(CH <sub>2</sub> Ph) <sub>2</sub> }] <sub>2</sub> TiMe <sub>2</sub>	50	101	2.9	2.02
[Ph <sub>2</sub> P{N( <i>p</i> -tolyl) <sub>2</sub> }] <sub>2</sub> ZrMe <sub>2</sub>	50	6900	19	2.68
[Ph <sub>2</sub> P{N( <i>p</i> -tolyl) <sub>2</sub> }] <sub>2</sub> ZrMe <sub>2</sub>	70	2900		
[Ph <sub>2</sub> P{N(CH <sub>2</sub> Ph) <sub>2</sub> }] <sub>2</sub> ZrMe <sub>2</sub>	70	2200	21.3	2.27

<sup>a</sup> Reaction conditions: catalyst 10 μmol, toluene 500 mL, MAO (Al/M = 2000, molar ratio), ethylene 75 psi (5.1 atm).

<sup>b</sup> Activity in kg polymer/mol M h.

<sup>c</sup> GPC data vs. polyethylene standard.

Table 11

Ethylene polymerization by Cp'TiX<sub>2</sub>(N=PR<sub>3</sub>) (Cp' = Cp, *tert*-BuCp; X = Cl, Me; R = Cy, <sup>i</sup>Pr, <sup>t</sup>Bu)–cocatalyst systems [47a]<sup>a</sup>

Complex	Cocatalyst	Activity <sup>b</sup>	$M_w^c$ ( $\times 10^{-4}$ )	$M_w/M_n^c$
CpTiCl <sub>2</sub> (N=PCy <sub>3</sub> )	MAO	42	0.36 33.6	1.8 2.2
CpTiCl <sub>2</sub> (N=P <sup>i</sup> Pr <sub>3</sub> )	MAO	49	1.87 57.9	2.8 2.4
CpTiCl <sub>2</sub> (N=P <sup>t</sup> Bu <sub>3</sub> )	MAO	500	8.99	2.4
CpTiMe <sub>2</sub> (N=PCy <sub>3</sub> )	Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub>	231	13.5	2.8
CpTiMe <sub>2</sub> (N=P <sup>i</sup> Pr <sub>3</sub> )	Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub>	225	16.4	3.4
CpTiMe <sub>2</sub> (N=P <sup>t</sup> Bu <sub>3</sub> )	Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub>	401	16.6	3.4
<sup>t</sup> BuCpTiCl <sub>2</sub> (N=PCy <sub>3</sub> )	MAO	46	0.74 89.4	2.1 3.4
<sup>t</sup> BuCpTiCl <sub>2</sub> (N=P <sup>i</sup> Pr <sub>3</sub> )	MAO	16	0.76 91	1.9 2.5
<sup>t</sup> BuCpTiCl <sub>2</sub> (N=P <sup>t</sup> Bu <sub>3</sub> )	MAO	881	6.54	2.4
<sup>t</sup> BuCpTiMe <sub>2</sub> (N=PCy <sub>3</sub> )	Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub>	1807	31	7.5
<sup>t</sup> BuCpTiMe <sub>2</sub> (N=P <sup>i</sup> Pr <sub>3</sub> )	Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub>	1193	25.9	9.9
<sup>t</sup> BuCpTiMe <sub>2</sub> (N=P <sup>t</sup> Bu <sub>3</sub> )	Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub>	1296	32.1	12.3
<sup>t</sup> BuCpTiMe <sub>2</sub> (N=P <sup>i</sup> Pr <sub>3</sub> )	MAO	853	5.56	2.3
[Me <sub>2</sub> Si(C <sub>5</sub> Me <sub>4</sub> )(N <sup>t</sup> Bu)]TiCl <sub>2</sub>	MAO	630		

<sup>a</sup> Conditions: catalyst 0.01–0.03 mmol, toluene, ethylene 1 atm, 25 °C, 0.5–3 min, MAO (Al/Ti = 500, molar ratio) or Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (B/Ti = 2).<sup>b</sup> Activity in kg polymer/mol Ti h.<sup>c</sup> GPC data vs. polyethylene standard.

Remarkably active, non-metallocene type titanium(IV) catalyst, (<sup>t</sup>Bu<sub>3</sub>P=N)<sub>2</sub>TiMe<sub>2</sub>, had been developed by Stephan et al. [47b] by replacing the cyclopentadienyl group into the phophinimide ligand according to the above strategy (Table 12). The observed activity would be the same as that by CGC, [Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(N<sup>t</sup>Bu)]TiMe<sub>2</sub>, under both high pressure and high temperature [160 °C, 1500 psi (102 atm)] conditions.

DFT calculations of the mechanism of polymerization for the series of catalyst models derived from CpTiMe<sub>2</sub>(N=PR<sub>3</sub>) (R = Me, NH<sub>2</sub>, H, Cl, F) demonstrated the critical role of ion pairing in determining the overall barrier to polymerization, and suggested that the ligands that incorporate electron-donating substituents would reduce the barrier [47f]. The tris-amidophosphinimide analogues, Cp'TiX<sub>2</sub>[N=P(NR<sub>2</sub>)<sub>3</sub>] (X = Cl, Me), showed notable catalytic activities upon the presence of borate-based activators (Table 13), and the activity increased upon increasing the steric bulk. Optimization of steric bulk and electronic characteristics to facilitate ion-pair separation and prolonged catalyst lifetime were thus achieved, affording a readily accessible and easily varied family of highly active catalysts.

Generally, the substituents on Cp' affect the catalytic activity [20,21,28c–e], because, as described above, the stabilization of the catalytically active species can be achieved by more electron donation through the cyclopentadienyl fragment. In contrast, no significant differences in the activities for ethylene polymerization using Cp'TiCl<sub>2</sub>(N=C'Bu<sub>2</sub>) [Cp' = Cp, *tert*-BuC<sub>5</sub>H<sub>4</sub>, Cp\*] were observed (Table 14) [51a]. The activities by CpTiCl<sub>2</sub>(N=CR<sub>2</sub>) were, however, strongly influenced by the substituents in the ketimide ligands (Table 15) [49], and these results clearly indicate that modification of the anionic ancillary donor ligands plays crucial role for exhibiting the high catalytic activity. Although distinct differences in the catalytic activities for ethylene polymerization with a series of the Cp'TiCl<sub>2</sub>(N=C'Bu<sub>2</sub>) were seen, the activities in the 1-hexene polymerizations were highly dependent upon the cyclopentadienyl fragment employed, as shown in Table 16. The polymerization by the Cp analogue, CpTiCl<sub>2</sub>(N=C'Bu<sub>2</sub>), took place efficiently, and a first order relationship between the monomer concentration and the reaction rate was seen based on time-course plots versus ln[M]/[M]<sub>0</sub>, strongly suggesting that

Table 12

Ethylene polymerization with (<sup>t</sup>Bu<sub>3</sub>P=N)<sub>2</sub>TiMe<sub>2</sub>–borate catalyst systems [47b]<sup>a</sup>

Complex (μmol)	Activator	Ethylene	Temperature (°C)	Activity <sup>b</sup>	$M_w^c$ ( $\times 10^{-4}$ )	$M_w/M_n^c$
( <sup>t</sup> Bu <sub>3</sub> P=N) <sub>2</sub> TiMe <sub>2</sub> (12.1)	Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub>	1 atm	25	1,166		
( <sup>t</sup> Bu <sub>3</sub> P=N) <sub>2</sub> TiMe <sub>2</sub> (2.31)	Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub>	1500 psi	160	18,950		
( <sup>t</sup> Bu <sub>3</sub> P=N) <sub>2</sub> TiMe <sub>2</sub> (0.58)	Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub>	1500 psi	160	62,310	7.75	1.9
[Me <sub>2</sub> Si(C <sub>5</sub> Me <sub>4</sub> )(N <sup>t</sup> Bu)]TiMe <sub>2</sub> (2.31)	Ph <sub>3</sub> CB(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub>	1500 psi	160	16,130	13.5	2.5

<sup>a</sup> Reaction conditions: cyclohexane, 1–3 min, ethylene 1 atm or 1500 psi (102 atm).<sup>b</sup> Activity in kg polymer/mol Ti h.<sup>c</sup> GPC data vs. polyethylene standards.

Table 13  
Polymerization testing of precatalysts, Cp'TiX<sub>2</sub>[NP(NR<sup>1</sup>R<sup>2</sup>)<sub>3</sub>] [47f]<sup>a</sup>

Precatalyst (μmol L <sup>-1</sup> )	Cocatalyst	Time (min)	Activity <sup>b</sup>	M <sub>n</sub> <sup>c</sup> (×10 <sup>-4</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>
CpTiCl <sub>2</sub> [N=P(NMe <sub>2</sub> ) <sub>3</sub> ] (100)	MAO	30	2.4	25.71	2.08
CpTiCl <sub>2</sub> [N=P(NEt <sub>2</sub> ) <sub>3</sub> ] (100)	MAO	30	26	12.99	3.57
CpTiCl <sub>2</sub> [N=P{N(Me) <sup>i</sup> Pr} <sub>3</sub> ] (50)	MAO	30	13	39.1	8.91
CpTiCl <sub>2</sub> [N=P{N(Et)Ph} <sub>3</sub> ] (50)	MAO	30	150	13.55	4.61
Cp <sup>*</sup> TiCl <sub>2</sub> [N=P(NMe <sub>2</sub> ) <sub>3</sub> ] (100)	MAO	30	21	82.6	1.72
Cp <sup>*</sup> TiCl <sub>2</sub> [N=P(NEt <sub>2</sub> ) <sub>3</sub> ] (100)	MAO	30	39	9.01	1.65
Cp <sup>*</sup> TiCl <sub>2</sub> [N=P{N(Me) <sup>i</sup> Pr} <sub>3</sub> ] (50)	MAO	30	56	12.78	2.76
Cp <sup>*</sup> TiCl <sub>2</sub> [N=P{N(Et)Ph} <sub>3</sub> ] (50)	MAO	30	200	12.61	4.02
CpTiMe <sub>2</sub> [N=P(NMe <sub>2</sub> ) <sub>3</sub> ] (4)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	2,200	31.5	2.05
CpTiMe <sub>2</sub> [N=P(NEt <sub>2</sub> ) <sub>3</sub> ] (4)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	3,500	39.4	1.91
CpTiMe <sub>2</sub> [N=P(NPr <sub>2</sub> ) <sub>3</sub> ] (4)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	5,500		
CpTiMe <sub>2</sub> [N=P(NBu <sub>2</sub> ) <sub>3</sub> ] (4)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	3,600		
CpTiMe <sub>2</sub> [N=P{N(Me) <sup>i</sup> Pr} <sub>3</sub> ] (4)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	3,600	38.86	1.85
CpTiMe <sub>2</sub> [N=P{N(Et)Ph} <sub>3</sub> ] (4)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	4,200	43.25	1.92
Cp <sup>*</sup> TiMe <sub>2</sub> [N=P(NMe <sub>2</sub> ) <sub>3</sub> ] (10)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	1,200		
Cp <sup>*</sup> TiMe <sub>2</sub> [N=P(NMe <sub>2</sub> ) <sub>3</sub> ] (4)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	4,200	14.08	4.92
Cp <sup>*</sup> TiMe <sub>2</sub> [N=P(NEt <sub>2</sub> ) <sub>3</sub> ] (10)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	2,000		
Cp <sup>*</sup> TiMe <sub>2</sub> [N=P(NEt <sub>2</sub> ) <sub>3</sub> ] (4)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	4,700		
Cp <sup>*</sup> TiMe <sub>2</sub> [N=P(NPr <sub>2</sub> ) <sub>3</sub> ] (4)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	10,000		
Cp <sup>*</sup> TiMe <sub>2</sub> [N=P(NBu <sub>2</sub> ) <sub>3</sub> ] (4)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	6,100		
Cp <sup>*</sup> TiMe <sub>2</sub> [N=P{N(Me) <sup>i</sup> Pr} <sub>3</sub> ] (10)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	2,100		
Cp <sup>*</sup> TiMe <sub>2</sub> [N=P{N(Me) <sup>i</sup> Pr} <sub>3</sub> ] (4)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	4,900	28.81	2.14
Cp <sup>*</sup> TiMe <sub>2</sub> [N=P{N(Et)Ph} <sub>3</sub> ] (10)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	2,300		
Cp <sup>*</sup> TiMe <sub>2</sub> [N=P{N(Et)Ph} <sub>3</sub> ] (4)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	4,200	32.46	2.03
Cp <sup>*</sup> TiMe <sub>2</sub> [N=P <sup>i</sup> Pr <sub>3</sub> ] (10)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	1,600		
Cp <sup>*</sup> TiMe <sub>2</sub> [N=P <sup>i</sup> Pr <sub>3</sub> ] (4)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	5,200	49.34	2.05
CpTiMe <sub>2</sub> [N=P <sup>i</sup> Bu <sub>3</sub> ] (10)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	2,900		
CpTiMe <sub>2</sub> [N=P <sup>i</sup> Bu <sub>3</sub> ] (4)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	5,600	43.78	1.8
Cp <sub>2</sub> ZrMe <sub>2</sub> (10)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	3,500		
Cp <sub>2</sub> ZrMe <sub>2</sub> (4)	Al <sup>i</sup> Bu <sub>3</sub> /B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	10	16,000	17.5	1.89

<sup>a</sup> Polymerization conditions: ethylene 2 atm at 30 °C, toluene 600 mL, stir rate = 1000 rpm, 500 equivalent of MAO, 2 equivalent of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>; 20 equivalent of Al<sup>i</sup>Bu<sub>3</sub>.

<sup>b</sup> Activity in kg PE/mol Ti h atm.

<sup>c</sup> GPC data in *o*-dichlorobenzene.

the apparent decrease is due to the decrease in the 1-hexene concentration not due to the deactivation of catalytically active species. As described below, although it is not clear enough to explain, and predict the effect of substituent on Cp' toward the desired polymerization, it is at least suggested that both Cp' and anionic donor ligand play an essential role for exhibiting the remarkable catalytic activities.

Kretschmer and Hessen reported that half-titanocenes containing 1,3-bis(xylyl)iminoimidazolidide ligand, CpTi(CH<sub>2</sub>Ph)<sub>2</sub>[N=C{N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)-CH<sub>2</sub>}<sub>2</sub>] (Scheme 6), exhibited notable catalytic activities for ethylene polymerization in the presence of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> cocatalyst [56]. As shown in Table 17, they emphasized that the catalyst showed higher catalytic activities than the CpTi(CH<sub>2</sub>Ph)<sub>2</sub>(NP<sup>i</sup>Bu<sub>3</sub>) under the same conditions (in

Table 14  
Ligand effect in ethylene polymerization by Cp'TiCl<sub>2</sub>(N=C'Bu<sub>2</sub>) (Cp' = Cp, <sup>i</sup>BuC<sub>5</sub>H<sub>4</sub>, Cp<sup>\*</sup>, indenyl)-MAO catalyst systems [51a]<sup>a</sup>

Cp'	Al/Ti <sup>b</sup> (×10 <sup>-3</sup> )	Ethylene (atm)	Polymer (yield/mg)	Activity <sup>c</sup>	M <sub>w</sub> <sup>d</sup> (×10 <sup>-5</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>d</sup>
Cp	10	4	317	9,500	9.85	1.9
Cp	15	4	445	13,400	9.66	1.9
Cp	15	6	737	22,100	9.84	1.9
<sup>i</sup> BuC <sub>5</sub> H <sub>4</sub>	10	4	379	11,400	12.6	2.0
<sup>i</sup> BuC <sub>5</sub> H <sub>4</sub>	15	4	477	14,300	9.9	2.1
Cp <sup>*</sup>	10	4	443	13,300	11.6	2.1
Cp <sup>*</sup>	15	4	552	16,600	10.4	2.2
Indenyl	10	4	248	7,400	5.59	2.2
Indenyl	15	4	255	7,700	5.61	2.1

<sup>a</sup> Conditions: complex 0.2 μmol, toluene 40 mL, MAO white solid, 40 °C, 10 min.

<sup>b</sup> Molar ratio of Al/Ti.

<sup>c</sup> Activity in kg PE/mol Ti h.

<sup>d</sup> GPC data in *o*-dichlorobenzene vs. polystyrene standards.

Table 15

Ethylene polymerization with Cp'TiX<sub>2</sub>(N=CR<sub>2</sub>) [Cp' = Cp, C<sub>5</sub>Me<sub>5</sub>, indenyl, C<sub>4</sub>Me<sub>4</sub>P; R = <sup>t</sup>Bu, NMe<sub>2</sub>, etc.]-MAO catalyst systems<sup>a</sup>

Complexes	Polymer (yield/g)	Activity (kg PE/mol Ti (or Zr) h)
CpTiCl <sub>2</sub> (N=C <sup>t</sup> Bu <sub>2</sub> )	5.08	668
CpTiCl <sub>2</sub> [N=C(NMe <sub>2</sub> )]	0.81	107
CpTiMe <sub>2</sub> [N=CPh(Me)]	0.84	111
(C <sub>5</sub> Me <sub>5</sub> )TiCl <sub>2</sub> (N=C <sup>t</sup> Bu <sub>2</sub> )	6.26	824
(Ind)TiCl <sub>2</sub> (N=C <sup>t</sup> Bu <sub>2</sub> )	13.02	1713
(C <sub>5</sub> Me <sub>4</sub> P)TiCl <sub>2</sub> (N=C <sup>t</sup> Bu <sub>2</sub> )	2.63	346
Ph <sub>2</sub> C(Flu)(Cp)ZrCl <sub>2</sub>	5.64	742
Cp <sub>2</sub> ZrCl <sub>2</sub>	20.18	2655

Slurry polymerization results [49].

<sup>a</sup> Conditions: catalyst 15.2 μmol, cyclohexane 300 mL, MAO (PMAO-IP), Al/M = 500, ethylene 10 psig (0.68 atm), 35 °C, 30 min.

the presence of partially hydrolyzed Al<sup>i</sup>Bu<sub>3</sub>, TIBAO). No polymerization results in the presence of MAO were introduced in the text [56].

Many additional attempts have been made to improve the activities by modification of the anionic ancillary donor ligands as shown in Scheme 7 (more recent examples). Zhang et al. reported that Cp<sup>\*</sup>TiCl<sub>2</sub>[N(<sup>t</sup>Bu)PPh<sub>2</sub>] showed moderate catalytic activities for ethylene polymerization in the presence of borate cocatalyst under optimized conditions, but the activity in the presence of MAO cocatalyst showed low activity (Table 18) [71].

Table 18

Ethylene polymerization by Cp<sup>\*</sup>TiCl<sub>2</sub>[N(<sup>t</sup>Bu)PPh<sub>2</sub>]-Al<sup>i</sup>Bu<sub>3</sub>-[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalyst system [71]<sup>a</sup>

Temperature (°C)	Al/Ti/B <sup>b</sup>	Yield (mg)	Activity <sup>c</sup>	M <sub>v</sub> (×10 <sup>-4</sup> )
20	2000 (MAO) <sup>d</sup>	80	64	7.8
20	1980/1/2	352	1564	60.1
20	150/1/1	151	671	33.1
20	150/1/2	383	1702	76.6
50	150/1/2	257	1142	48.9
70	150/1/2	213	947	33.0
20	200/1/2	566	2516	81.1

<sup>a</sup> Conditions: Ti 2.7 μmol, ethylene 1 atm, toluene 50 mL, 5 min.<sup>b</sup> Molar ratio.<sup>c</sup> Activity in kg PE/mol Ti h.<sup>d</sup> MAO was used.

Use of bulky alkoxide ligands in place of aryloxides was also explored, and Hierro et al. prepared CpTiCl<sub>2</sub>(OR) (R = OAdam, Oment, Oorn, etc.) by reaction of CpTiCl<sub>3</sub> with bulky alcohol such as 1-adamantanol (AdamOH), (1R, 2S, 5R)-menthol (MentOH), (1S-endo)-borneol (BornOH), in the presence of NEt<sub>3</sub> [76]. However, the observed catalytic activities were low in all cases, suggesting that this approach may not be suited to find an efficient catalyst. Related approaches were taken recently, but some manuscripts only introduced styrene polymerization results without description of the ethylene polymerization results probably due to the low activities. Another approach in this topic

Table 16

1-Hexene polymerization by Cp'TiCl<sub>2</sub>(N=C<sup>t</sup>Bu<sub>2</sub>) (Cp' = Cp, <sup>t</sup>BuC<sub>5</sub>H<sub>4</sub>, Cp<sup>\*</sup>, indenyl)-MAO catalyst systems [51a,b]<sup>a</sup>

Cp' (μmol)	MAO (mmol) (Al/Ti × 10 <sup>-2</sup> ) <sup>b</sup>	Time (min)	Polymer (yield/mg)	Activity <sup>c</sup>	TON (×10 <sup>-3</sup> )	M <sub>w</sub> <sup>d</sup> (×10 <sup>-4</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>d</sup>
Cp (0.25)	2.0 (80.0)	5	782	37500	37.2	60.0	1.6
Cp (0.25)	2.0 (80.0)	10	985	23600	46.9	59.5	1.6
Cp (0.25)	2.0 (80.0)	20	1403	16800	66.8	61.7	1.6
Cp (0.25)	3.0 (120)	20	1380	16600	65.7	55.2	1.8
<sup>t</sup> BuC <sub>5</sub> H <sub>4</sub> (2.5)	2.0 (8.00)	20	1094	1310	5.21	28.5	1.7
<sup>t</sup> BuC <sub>5</sub> H <sub>4</sub> (2.5)	3.0 (12.0)	20	1036	1240	4.93	29.6	1.6
Cp <sup>*</sup> (2.5)	2.0 (8.00)	20	474	569	2.26	13.0	1.6
Cp <sup>*</sup> (2.5)	3.0 (12.0)	20	449	539	2.14	12.0	1.6
Indenyl (0.25)	2.0 (8.00)	20	994	11900	47.2	28.1	1.7
Indenyl (0.25)	3.0 (12.0)	20	1060	12700	50.4	26.6	1.7

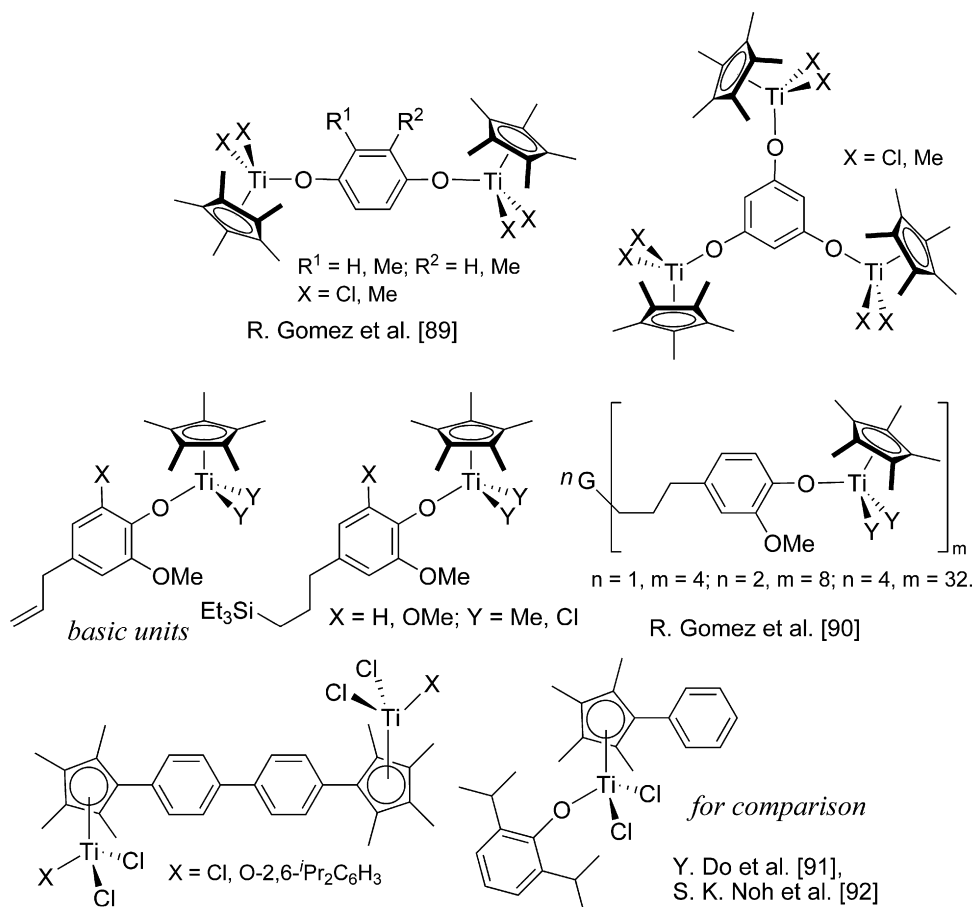
<sup>a</sup> Conditions: complex in toluene 0.5 mL, 1-hexene 10 mL, 25 °C, MAO white solid (prepared by removing toluene and AlMe<sub>3</sub> from ordinary MAO), 25 °C, 20 min.<sup>b</sup> Molar ratio of Al/Ti.<sup>c</sup> Activity in kg polymer/mol Ti h.<sup>d</sup> GPC data in THF vs. polystyrene standards.

Table 17

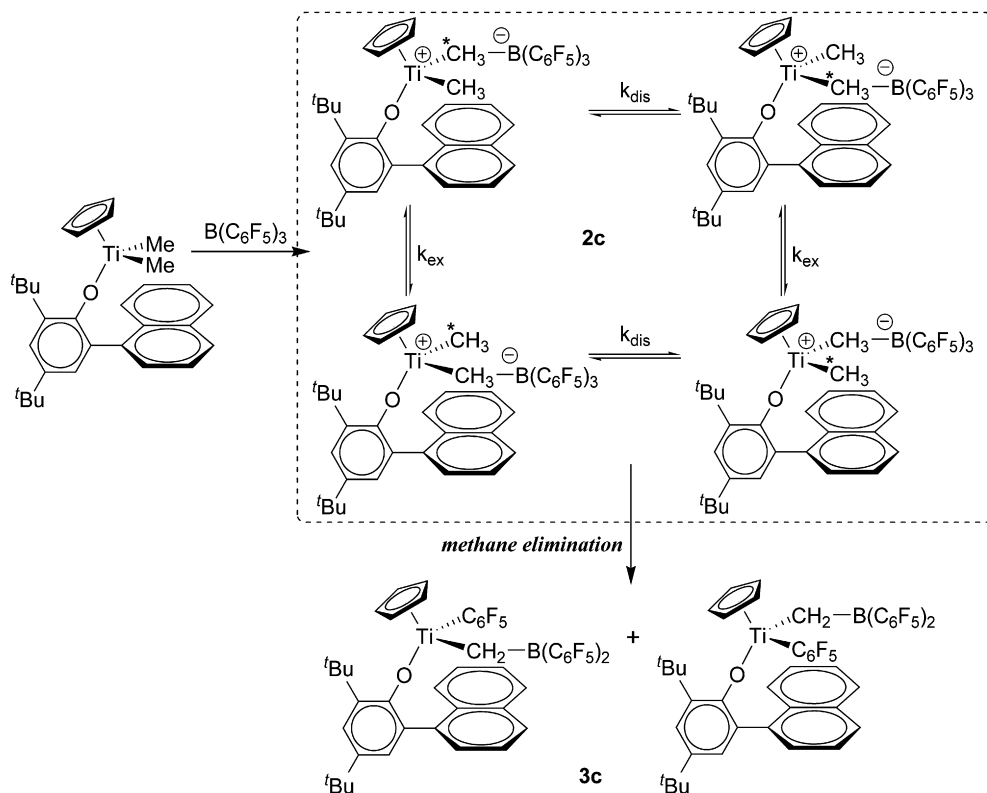
Ethylene polymerization with CpTi(CH<sub>2</sub>Ph)<sub>2</sub>(L)-cocatalyst systems [56]<sup>a</sup>

L	Cocatalyst	Activity (kg PE/mol Ti h bar)	M <sub>w</sub> <sup>b</sup> (×10 <sup>-5</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>
N=C[N(CH <sub>2</sub> ) <sub>5</sub> ] <sub>2</sub>	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	376	4.06	1.9
N=C[N(CH <sub>2</sub> ) <sub>5</sub> ] <sub>2</sub>	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /TIBAO	32	5.83	1.7
N=C[N(CH <sub>2</sub> ) <sub>2</sub> (2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> ]	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	896	3.61	1.9
N=C[N(CH <sub>2</sub> ) <sub>2</sub> (2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) <sub>2</sub> ]	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /TIBAO	1600	6.63	2.2
N=C <sup>t</sup> Bu <sub>2</sub>	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	353	5.43	1.9
N=P <sup>t</sup> Bu <sub>3</sub>	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	848	5.18	2.2
N=P <sup>t</sup> Bu <sub>3</sub>	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> /TIBAO	1128	7.17	2.1

<sup>a</sup> Conditions: Ti 10 μmol, Al/B/Ti = 20/1.1/1.0 (molar ratio), ethylene 5 bar, 80 °C, 15 min, toluene 210 or 260 mL.<sup>b</sup> GPC data vs. polystyrene standards.



Scheme 10. Examples for synthesis of multinuclear half-titanocenes.

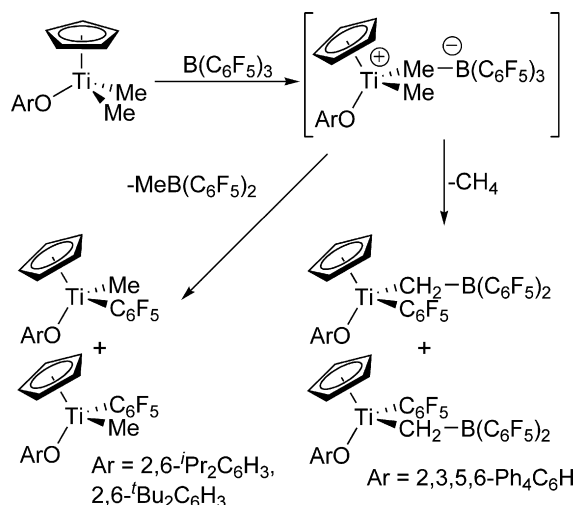
Scheme 11. Reaction of  $\text{CpTiMe}_2(\text{OAr})$  with  $\text{B}(\text{C}_6\text{F}_5)_3$  in toluene ( $\text{OAr} = \text{O}-4,6\text{-}^t\text{Bu}_2\text{-2-naphthyl-C}_6\text{H}_2$ ) [93].

is to use dimeric, supported on dendrimer as shown in Scheme 10 [89–92]. These approaches would introduce new possibilities in this research field.

### 2.3. Some chemistry related to olefin polymerization using half-titanocenes

As described above, addition of  $B(C_6F_5)_3$  into a benzene solution containing  $CpTiMe_2(OAr)$  complex containing *ortho*-naphthylphenoxide ligand prepared by Rothwell et al. gave thermally unstable cationic complex (2), then decomposed at ambient temperature affording the neutral species (3) by methane elimination (Scheme 9) [84]. Toluene- $d_8$  solutions containing 2 [Ar = 2,6-Ph<sub>2</sub>-3,5-Me<sub>2</sub>C<sub>6</sub>H (a), 4,6-<sup>*t*</sup>Bu<sub>2</sub>-2-PhC<sub>6</sub>H<sub>2</sub> (b), 4,6-<sup>*t*</sup>Bu<sub>2</sub>-2-naphthyl-C<sub>6</sub>H<sub>2</sub> (c), 2,3,5,6-Ph<sub>4</sub>C<sub>6</sub>H (d)] eliminated methane at a rate which was temperature dependent to afford the corresponding neutral species 3 monitored by <sup>1</sup>H NMR spectra [93]. Related reactivity was been observed for the decomposition of other cationic methyl compounds of the group 4 metals where  $[MeB(C_6F_5)_3]^-$  anions are present, and in a particularly important mechanistic study, it was concluded that the reaction occurs via a  $\sigma$ -bond metathesis pathway [50a], reported by Piers et al. as described below. In the <sup>1</sup>H NMR spectra of the neutral species derived from 2a–b, d, a single set of Cp and aryloxy resonances was present along with well-resolved, diastereotopic Ti–CH<sub>2</sub>–B protons. In contrast, two sets of sharp NMR signals are present in the case of  $[CpTiMe(OAr)]^+[MeB(C_6F_5)_3]^-$  containing the chiral *o*-(1-naphthyl) ligand (3c), due to a 70:30 mixture of the two possible diastereomers (Scheme 11). The fact that exchange of these isomers was slow on the NMR time scale at ambient temperature confirmed that naphthyl rotation could not account for the observed fluxionality in 2c. A kinetic study showed a first order decomposition of 2d over approximately 4 half-lives (the rate constant of  $7.62 \times 10^{-4} \text{ s}^{-1}$  at 25.0 °C,  $t_{1/2} = 15 \text{ min}$ ) [93].

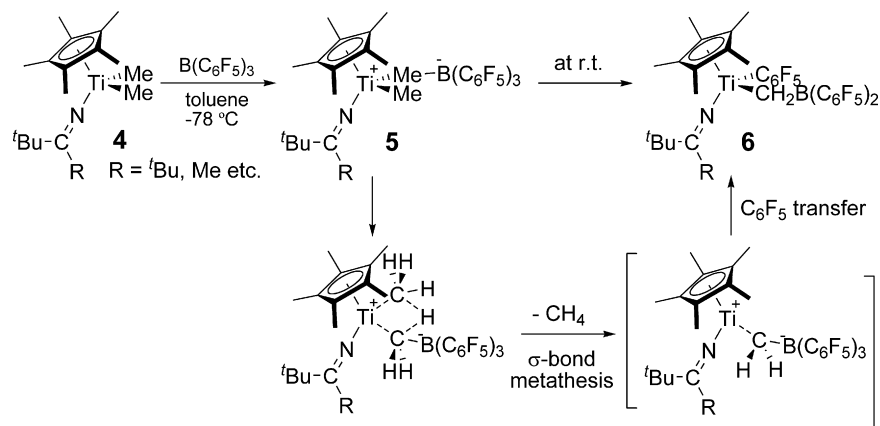
The further research revealed that Me/C<sub>6</sub>F<sub>5</sub> exchange affording  $CpTiMe(C_6F_5)(OAr)$  took place in the reaction of  $CpTiMe_2(OAr)$  with  $B(C_6F_5)_3$  if the reactions were employed with relatively small aryloxy ligands (Ar = 2,6-<sup>*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,6-<sup>*t*</sup>Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), whereas 2c decomposed to afford 3c accompanied by formation of methane (Scheme 12) [94]. As described above,



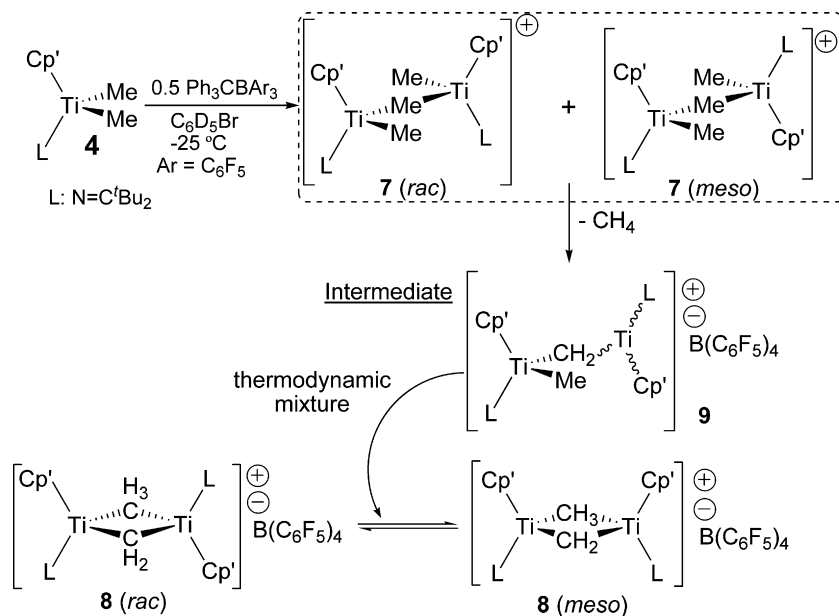
Scheme 12. Two possible pathways for reaction of  $CpTiMe_2(OAr)$  with  $B(C_6F_5)_3$  [94].

the reaction of  $Cp^*TiMe_2(O-2,6-<sup>*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)$  (1b) with  $B(C_6F_5)_3$  in toluene- $d_8$  afforded  $Cp^*Ti(C_6F_5)[CH_2B(C_6F_5)_2](O-2,6-<sup>*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)$  (and/or intermediates) even at  $-70^\circ\text{C}$  [85]. The reaction pathway [methane elimination or Me/C<sub>6</sub>F<sub>5</sub> exchange] would be thus highly dependent upon the steric/electronic nature of both cyclopentadienyl and anionic donor ligands employed.

The detailed studies for methane elimination mechanism of (cyclopentadienyl)(ketimide)titanium(IV) complex of the type,  $Cp^*TiMe_2[N=C^tBu(R)]$  [ $Cp^* = Cp, Cp^*, C_5Me_4(SiMe_3)$ ;  $R = <sup>*t*</sup>Bu, Me, CH_2SiMe_3$ ] was made by Piers et al. [50]. They isolated cationic species 5 and fully identified by <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F and <sup>11</sup>B NMR as well as by elemental analysis (Scheme 13). Based on the result of deuterium labeling crossover experiment with  $B(C_6F_5)_3$  using a mixture of dimethyl (4) and deuterated dimethyl ( $d_6$ -4) complexes, they showed that the reaction proceeded via intramolecular pathway for methane elimination because no scrambling of the methyl group to produce isotopomers were observed. Only CH<sub>4</sub> and CD<sub>4</sub> were detected by <sup>1</sup>H and <sup>2</sup>H NMR, if the above solution was allowed to decompose, strongly implying an intramolecular pathway for methane elimination. The latter pathway was also confirmed by kinetic studies carried out by monitoring the reaction using <sup>1</sup>H NMR in toluene- $d_8$ .

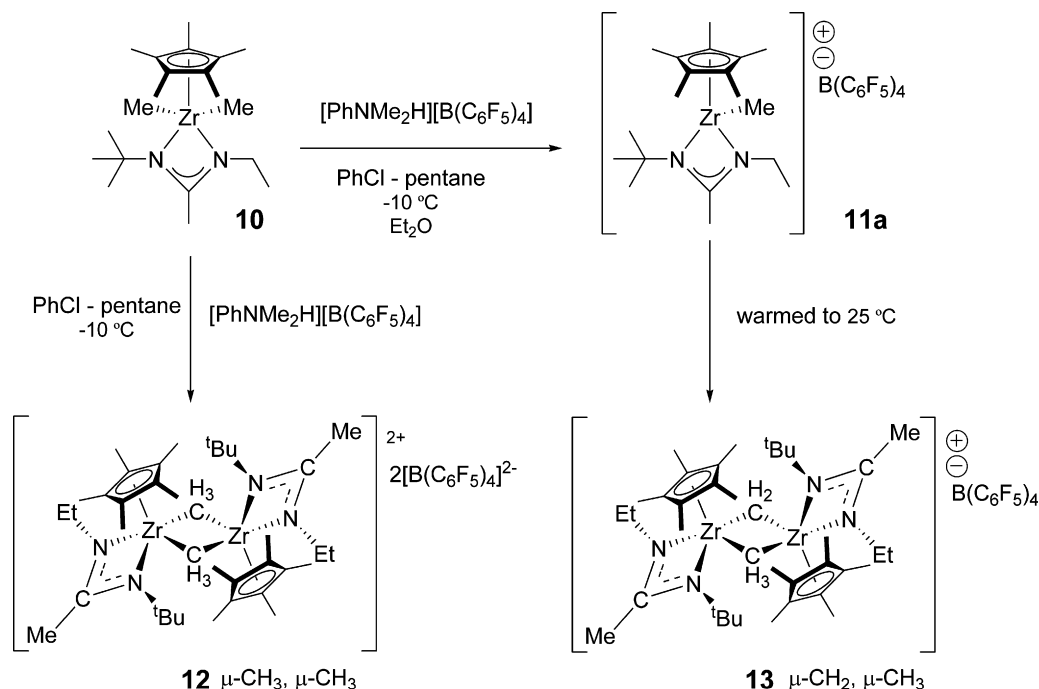


Scheme 13. Reaction of  $Cp^*TiMe_2[N=C^tBu(R)]$  ( $R = \text{Me}, <sup>*t*</sup>\text{Bu}$ ) with  $B(C_6F_5)_3$  [50a].

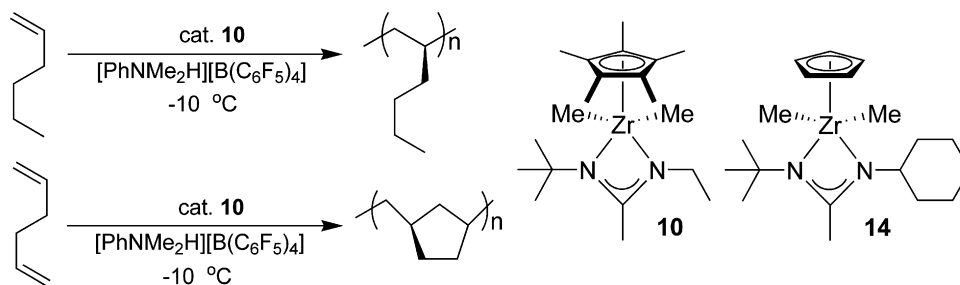
Scheme 14. Reaction of  $\text{Cp}'\text{TiMe}_2(\text{N}=\text{C}'\text{Bu}_2)$  with 0.5 equiv. of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  [50b].

The methane elimination process for ion pair of **5** affording **6** was proved to proceed via  $\sigma$ -bond metathetical elimination of methane from a contact ion pair. The possibility for borane dissociation and/or ion-pair dissociation could be excluded, because only  $\text{SiMe}_4$  was formed from the cationic species,  $[\text{Cp}^*\text{Ti}(\text{CH}_2\text{SiMe}_3)(\text{N}=\text{C}'\text{Bu}_2)]^+ [\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ , that were generated exclusively by the reaction of  $\text{Cp}^*\text{TiMe}(\text{CH}_2\text{SiMe}_3)(\text{N}=\text{C}'\text{Bu}_2)$  with  $\text{B}(\text{C}_6\text{F}_5)_3$  [50a]. The mechanism from **5** to **6** could be thus explained by 1)  $\sigma$ -bond metathesis of **5** affording zwitter ionic intermediate,  $[\text{Ti}^+-\text{CH}_2-\text{B}(\text{C}_6\text{F}_5)_3]$ , 2) then  $\text{C}_6\text{F}_5$  transfer affording final product, **6** (Scheme 13) [50a].

The reaction of **4** with 0.5 equivalent of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in bromobenzene- $d_5$  at  $-25^\circ\text{C}$  gave binuclear  $\mu$ -methyl monocationic species, **7**, with 1:1 mixture of *rac/meso* form (Scheme 14). Upon warming the reaction mixture upto room temperature gave another monocationic species,  $\{[\text{Cp}(\text{L})\text{Ti}]_2(\mu\text{-CH}_2)(\mu\text{-CH}_3)\}^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$  (**8**) exclusively [50b]. While the loss of methane from *rac/meso* **7** ( $\text{Cp}' = \text{Cp}^*$  and  $\text{C}_5\text{Me}_4\text{SiMe}_3$ ) proceeded with >95% diastereoselectivity to *rac* **8** dominating, the dimers were formed as a mixture of diastereomers in the Cp compounds, presumably with *rac* **8** dominating (*rac/meso* = 7/3), suggesting a thermodynamic control was oper-

Scheme 15. Formation of cationic species derived from **10** [95a].





Scheme 16. Isospecific living polymerization of 1-hexene, 1,5-hexadiene by “exposed” zirconium acetamidinate complexes [55a,c].

ating. In addition, dissociation of dimer took was very slow as confirmed by deuterium labeling crossover experiment. Methane loss likely proceeds via  $\sigma$ -bond metathesis involving a C–H bond of the bridging methyl group, in a reaction similar to that observed in **5**. The equilibration of the resulting diastereomers should be possible since then the intermediate **9** should be able to undergo epimerization at titanium and/or rotation about the Ti–CH<sub>2</sub><sup>+</sup> bond (Scheme 14) [50b].

As described below, half-zirconocene containing acetamidinate ligand (**10**) initiates isospecific living polymerization of 1-hexene [55a], and the same complex also initiates living cyclopolymerization of 1,5-hexadiene [55c]. Monocationic methyl species, Cp<sup>\*</sup>ZrMe[<sup>t</sup>BuNC(Me)NEt][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**11a**) could be isolated, and was fully characterized as the Et<sub>2</sub>O adduct, if Cp<sup>\*</sup>ZrMe<sub>2</sub>[N<sup>t</sup>BuNC(Me)NEt] (**10**) was treated with 1 equivalent of [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in PhCl at –10 °C upon the presence of Et<sub>2</sub>O in trace amount (Scheme 15) [93a]. Moreover, dicationic dimeric  $\mu$ -CH<sub>3</sub>,  $\mu$ -CH<sub>3</sub> complex (**12**) could also be isolated after several days, if the reaction was performed without Et<sub>2</sub>O (Lewis base). Monocationic, dimeric  $\mu$ -CH<sub>2</sub>,  $\mu$ -CH<sub>3</sub> complex of **13** could also be isolated upon warming the reaction mixture containing **11a** to room temperature. An increase in the acidity of the bridging methyl groups that occur upon formation of **12a** might induce deprotonation by the PhNMe<sub>2</sub> (that remains after demethylation of the dimethyl species) to afford **13**. In this sense, similar deprotonation of dimers formed from propagating species could represent a terminating event during polymerization. Formation of the dimer (**12**) suggested that the similar dimers might play a role as the propagating species in metal catalyzed olefin polymerization system. This species possessed bridging *agostic* interactions that would be supposed to lower the barriers for steps involved in both propagation and termination. In addition, the dimers of propagating species would also serve as dormant, stable, resting states in the polymerization system.

#### 2.4. Isospecific living polymerization of $\alpha$ -olefins and the related chemistry

Half-zirconocene containing acetamidinate ligand (**10**) initiates isospecific living polymerization of 1-hexene [55a], and the same complex also initiated living cyclopolymerization of 1,5-hexadiene [55c] (Scheme 16). The Cp analogue (**14**) prepared also initiated isospecific living polymerization of vinylcyclohexane [55d]. The 1-hexene polymerization afforded high molecular

weight isotactic (mmmm >95%) polymers with narrow molecular weight distribution ( $M_n = 69544$ ,  $M_w/M_n = 1.10$ ), and the linear plots between  $M_n$  and conversion of 1-hexene without changing  $M_w/M_n$  values were obtained. Moreover, the resultant polymer possessed narrow molecular weight distribution by additional 1-hexene after consumption of previous monomer (called post polymerization), and these facts strongly indicated that the polymerization took place in a living manner. The origin of high isospecificity by **10**/[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] should be due to that site-isomerization after olefin insertion must occur more rapidly than olefin complexation and propagation [55a].

Effect of substituent on the amidinate ligands toward the activity, stereospecificity, as well as the living character was explored in the 1-hexene polymerization with the various half-zirconocenes, [Cp<sup>\*</sup>ZrMe{N(R<sup>1</sup>)C(R<sup>3</sup>)N(R<sup>2</sup>)}]<sup>+</sup>, as shown in Table 19 [55e]. Although the living polymerization character was observed in the polymerization by **11c** (only R<sup>3</sup> was replaced from Me to Ph), significant loss of the stereoregularity was confirmed by the <sup>13</sup>C NMR spectrum. The *tert*-Bu analogue (**11d**) did not show the catalytic activity, and the polymerization did not proceed in a living manner with loss of the stereo control if **11b** was used in place of **11a**. A distinct Goldilocks effect was thus observed where fine balance between nonliving character and no activity is controlled by the steric bulk of the distal amidinate substituent. The loss of stereo control should be due to the two different mechanisms depending upon the steric bulk of the distal amidinate substituent: a low barrier to metal-centered epimerization observed by **11b**, and a lack of steric discrimination at the metal center for olefin coordination observed by **11c** [55e].

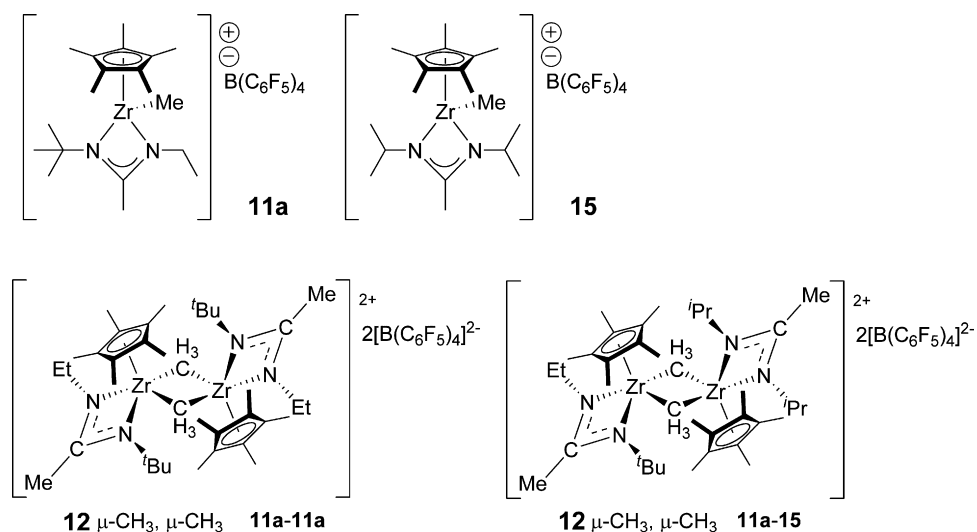
The methyl scrambling between monocationic species (**11a**) and the other monocationic species (**15**) was occurred

Table 19  
1-Hexene polymerization by half-zirconocene containing various amidinate ligands, [Cp<sup>\*</sup>ZrMe{N(R<sup>1</sup>)C(R<sup>3</sup>)N(R<sup>2</sup>)}]<sup>+</sup> [55e]<sup>a</sup>

R <sup>1</sup> ; R <sup>2</sup> ; R <sup>3</sup>	Yield (%)	$M_n^b$	$M_w/M_n^b$
<sup>t</sup> Bu; Et; Me ( <b>11a</b> )	95	19,800	1.03
<sup>t</sup> Bu; Et; H ( <b>11b</b> )	45	20,100	1.59
<sup>t</sup> Bu; Et; Ph ( <b>11c</b> )	90	19,300	1.02
<sup>t</sup> Bu; Et; <sup>t</sup> Bu ( <b>11d</b> )	Inactive		
<sup>i</sup> Pr; <sup>i</sup> Pr; H ( <b>11e</b> )	98	25,100	1.23

<sup>a</sup> Conditions: Zr 2.5  $\mu$ mol, 200 equivalent of 1-hexene, chlorobenzene at –10 °C for 2 h.

<sup>b</sup> GPC data in THF vs. polystyrene standards.



Scheme 17. Rapid scrambling of the methyl group between **11a** and **15** via dimeric intermediates (**12**, **12'**) [95b].

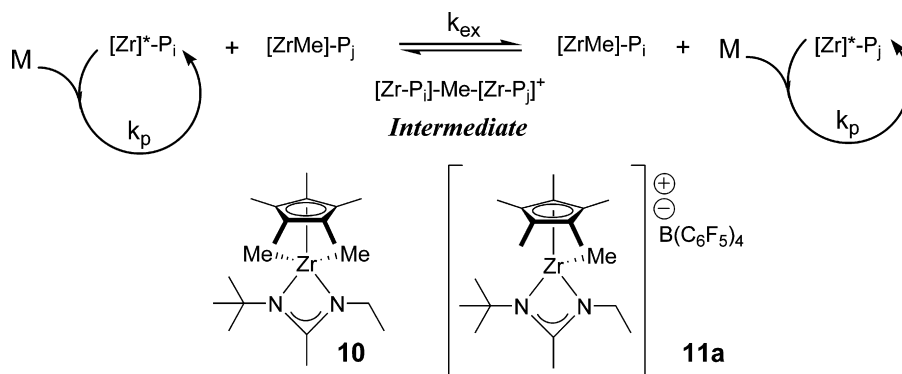
(Scheme 17), and the result clearly indicate that rapid transfer of a highly 'stereoregular' alkyl (polymer) chain to a 'nonstereospecific' propagating center via methyl-polymeryl exchange was present [95b]. These would provide the new strategy for synthesis of well-defined stereoblock polymers in a living manner [95b].

Polymerization of 1-hexene with **10** with 0.5 equivalent of  $[PhNMe_2H][B(C_6F_5)_4]$  at  $-10^\circ C$  afforded isotactic-rich poly(1-hexene) ( $mm = 25\%$ ), whereas the polymerization with 1.0 equivalent of borate afforded isotactic poly(1-hexene) as reported [55a]. A process of *degenerative transfer* involving rapid and reversible alkyl group exchange between cationic (active) zirconium propagating centers and neutral (dormant) methyl, polymeryl Zr end groups was thus considered as the mechanism in this living polymerization system as shown in Scheme 18 [95c]. Facile metal centered epimerization of dormant species was thus responsible for loss of stereo-control during propagation that produces isotactic-rich materials, whereas the pure isotactic polymer was obtained if the degenerative transfer process was not present (molar ratio of borate/Zr > 1). The stereoblock material, *atactic*-poly(1-hexene)-*b*-*isotactic*-poly(1-octene), was thus prepared according to the procedure shown in Scheme 19 based

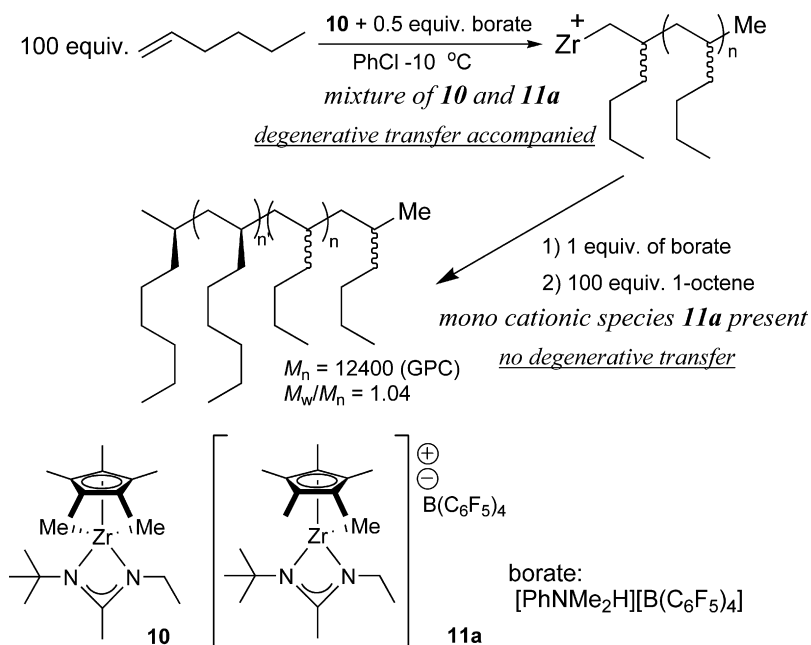
on the above facts. The successful realization of a stereospecific chloride degenerative transfer living Ziegler-Natta polymerization process that provides isotactic polyolefins of narrow polydispersity could be thus achieved if the  $Cp^*ZrCl(isobutyl)[N^iBuC(Me)NEt]$  was employed in place of the dimethyl analogue [95d].

### 2.5. Modification of ligands for syndiospecific styrene polymerization

As described above (shown in Scheme 3), ordinary Ziegler-Natta catalysts, metallocenes, linked half-titanocenes like  $[Me_2Si(C_5Me_4)(N^iBu)]TiCl_2$  (CGC), exhibit high catalytic activities for olefin polymerization [4,5,13]. However, these catalysts generally show extremely low (or negligible) catalytic activities for styrene polymerization [13d,96]. In contrast, it is well known that half-titanocenes such as  $Cp^*Ti(OMe)_3$ ,  $Cp^*TiCl_3$ ,  $Cp^*TiF_3$  exhibit remarkable catalytic activity for syndiospecific styrene polymerization (Scheme 3) [28]. However, these complexes are not efficient catalyst precursors for olefin polymerization. The facts might suggest that basic design (catalytically active species, oxidation state) between olefin polymerization and styrene polymerization should be different.



Scheme 18. Degenerative transfer living polymerization involving rapid and reversible methyl group exchange between cationic (active) zirconium propagating centers and neutral (dormant) methyl, polymeryl zirconium species [95c].



Scheme 19. Synthesis of stereoblock copolymer in a living manner [95c].

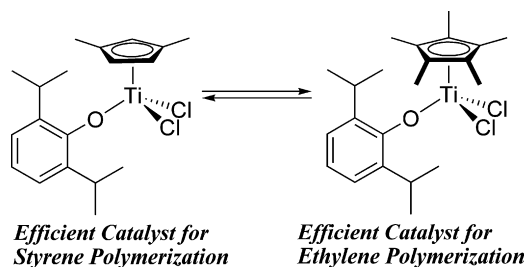
In contrast, the efficient catalyst for syndiospecific styrene polymerization by (aryloxo)(cyclopentadienyl)titanium complex catalysts, can be modified from the efficient catalyst for olefin polymerization only by modification of substituent on Cp' (Scheme 20); (1,3-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>)TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and (t-BuC<sub>5</sub>H<sub>4</sub>)TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) exhibited high catalytic activities for styrene polymerization affording high molecular weight syndiotactic polystyrene exclusively [35]. This displayed one of the most unique characteristics for using this type of complexes as the olefin polymerization catalysts.

(t-BuC<sub>5</sub>H<sub>4</sub>)TiCl<sub>2</sub>(OAr) exhibited moderate catalytic activity for syndiospecific styrene polymerization at 25 °C when both [PhMe<sub>2</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and a mixture of Al<sup>*i*</sup>Bu<sub>3</sub>/Al(*n*-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub> were used as the cocatalyst, and the activities with a series of (1,3-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>)TiCl<sub>2</sub>(OAr) highly depended on the aryloxo ligand used [97]. The fact is an interesting contrast to the reported facts by Baird et al. that the reaction of Cp\*TiMe<sub>3</sub> with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in hexane/toluene mixed solvent gave Cp\*TiMe<sub>2</sub>(μ-Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> which initiated polymerization of isobutene, vinyl ethers, N-vinylcarbazole [29,30,98], and they demonstrated that these polymerization took place not by coordination/migration polymerization mechanism but by carbocationic polymerization mechanism. In addition, the styrene polymerization in *n*-hexane

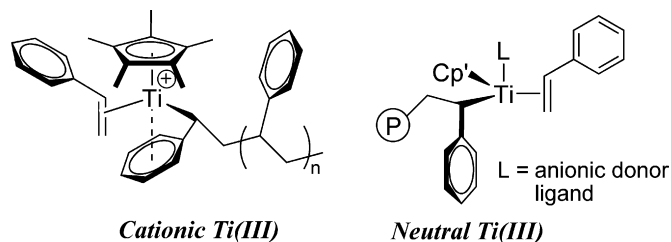
or in bulk gave syndiotactic polystyrene in good yields containing atactic polymer, whereas the ratio of *s*-PS/*a*-PS depended on polymerization temperature if the polymerization was performed in toluene.

Although role of the anionic ancillary ligand (aryloxo, amide, anilide) should be negligible according to the assumption that cationic Ti(III), [Cp'Ti(R)(styrene)]<sup>+</sup> (R = polymer, alkyl chain) plays an essential role for the syndiospecific styrene polymerization [28,99], the electronic and/or steric nature of the anionic ancillary donor ligand affected the catalytic activity in the above styrene polymerization [35,97], as Tomotsu et al. also insisted the possibility that neutral Ti(III) species, [Cp'Ti(L)(R)(styrene)] (L = anionic donor ligand), plays an important role as the catalytically active species (Scheme 21) [28d–e].

Effect of both the cyclopentadienyl and the anionic donor ligands in syndiospecific styrene polymerization with a series of half-titanocenes of the type, Cp'TiCl<sub>2</sub>(L) [Cp' = Cp, 1,3-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>, 1,2,4-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub>, Cp\*]; L = OPh, O-4-MeC<sub>6</sub>H<sub>4</sub>, O-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, O-2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, NMeCy, N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(SiMe<sub>3</sub>), N=C<sup>*t*</sup>Bu<sub>2</sub>] in the presence of MAO [35b,51a]. As shown in Table 20 and Fig. 2, the catalytic activities for syndiospecific styrene polymerization with a series of



Scheme 20. Modification of efficient catalyst between olefin and syndiospecific styrene polymerization [35a].



Scheme 21. Proposed two catalytically active species for syndiospecific styrene polymerization by half-titanocenes [28d,e].

Table 20  
Effect of aryloxy ligand in styrene polymerization by  $\text{Cp}^*\text{TiCl}_2(\text{X})$ –MAO catalyst systems [35b,51a]<sup>d</sup>

X	Temperature (°C)	Activity <sup>b</sup>	$M_w^c$ ( $\times 10^{-4}$ )	$M_w/M_n^c$
Cl (2.0)	40	320	36.2	2.3
Cl (2.0)	55	1640	33.2	2.3
Cl (2.0)	70	1970	24.8	2.5
Cl (2.0)	85	3280	17.5	2.2
O-2,6- <i>i</i> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (2.0)	40	285	26.8	2.6
O-2,6- <i>i</i> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (2.0)	55	1640	53.1	2.5
O-2,6- <i>i</i> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (2.0)	70	3600	49.0	2.2
O-2,6- <i>i</i> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (2.0)	85	4290	32.3	2.2
OC <sub>6</sub> H <sub>5</sub> (2.0)	40	733	55.1	2.2
OC <sub>6</sub> H <sub>5</sub> (2.0)	55	1600	55.1	2.0
OC <sub>6</sub> H <sub>5</sub> (2.0)	70	4170	54.3	2.0
OC <sub>6</sub> H <sub>5</sub> (2.0)	85	6390	47.8	2.1
O-4-MeC <sub>6</sub> H <sub>4</sub> (2.0)	40	757	30.4	2.8
O-4-MeC <sub>6</sub> H <sub>4</sub> (2.0)	55	1560	28.7	2.3
O-4-MeC <sub>6</sub> H <sub>4</sub> (2.0)	70	3750	26.7	2.4
O-4-MeC <sub>6</sub> H <sub>4</sub> (2.0)	85	6020	24.2	2.3
O-2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (2.0)	40	1020	30.1	2.3
O-2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (2.0)	55	4090	29.6	2.0
O-2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (2.0)	70	9200	28.0	2.1
O-2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (2.0)	85	12400	20.7	2.1
O-2,6- <i>t</i> Bu <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (2.0)	40	75	11.0	1.9
O-2,6- <i>t</i> Bu <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (2.0)	55	279	11.4	2.1
O-2,6- <i>t</i> Bu <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (2.0)	70	1780	20.5	2.3
O-2,6- <i>t</i> Bu <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (2.0)	85	5690	23.1	2.2
N=C <sup><i>t</i></sup> Bu <sub>2</sub> <sup>d</sup>	25	22.6	13.1	2.2
N=C <sup><i>t</i></sup> Bu <sub>2</sub> (0.4) <sup>d</sup>	40	245	5.1	1.6
N=C <sup><i>t</i></sup> Bu <sub>2</sub> (0.4) <sup>d</sup>	60	740	5.6	1.4
N=C <sup><i>t</i></sup> Bu <sub>2</sub> (0.4) <sup>d</sup>	80	1790	5.5	1.4

<sup>a</sup> Conditions: catalyst 2.0  $\mu\text{mol}$  styrene/toluene = 10/20 mL, MAO white solid 3.0 mmol (Al/Ti = 1500, molar ratio), 10 min.

<sup>b</sup> Activity in kg *s*-PS/mol Ti h.

<sup>c</sup> GPC data in *o*-dichlorobenzene vs. polystyrene standard.

<sup>d</sup> Styrene/toluene = 1/10 mL, 30 min.

$\text{Cp}^*\text{TiCl}_2(\text{L})$  were dependent upon the anionic donor ligand employed. The catalytic activities increased at higher temperature, and the molecular weights for resultant syndiotactic polystyrenes were dependent upon the anionic donor ligand employed. As also shown in Table 21, the catalytic activities with a series of the *tert*-BuCp analogues were also dependent upon the anionic donor ligand [81,51a], and, as described above, the activi-

ties with (1,3-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>)TiCl<sub>2</sub>(OAr)–[PhMe<sub>2</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalysts in the presence of Al<sup>*t*</sup>Bu<sub>3</sub>/Al(*n*-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub> were highly dependent on the aryloxy ligand used [97]. The role of the anionic donor ligand, like the aryloxy ligand, toward both the catalytic activity and the  $M_w$  values of polystyrene was thus observed irrespective of kind of cocatalyst employed [35b]. Although it has been invoked that cationic Ti(III) plays an essential role for syndiospecific styrene polymerization, the role of anionic donor

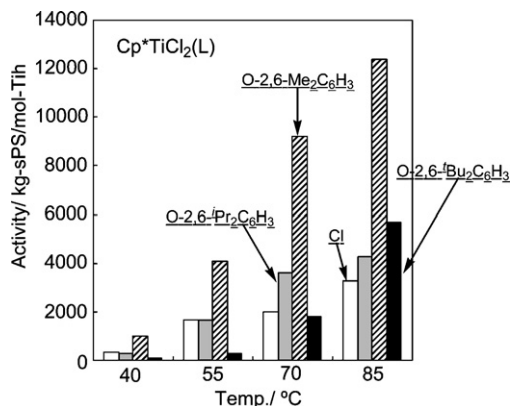


Fig. 2. Temperature dependence toward catalytic activity for syndiospecific styrene polymerization catalyzed by  $\text{Cp}^*\text{TiCl}_2(\text{L})$  (L = Cl, O-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, O-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, O-2,6-*t*Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)–MAO catalyst systems (shown in Table 20) [35b].

Table 21  
Effect of aryloxy ligand for styrene polymerization by (*t*BuC<sub>5</sub>H<sub>4</sub>)TiCl<sub>2</sub>(L)–MAO catalyst systems [81,51a]<sup>d</sup>

L	Activity <sup>b</sup>	$M_n^c \times 10^{-4}$	$M_w/M_n^c$
O-2,6-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	1370	5.3	2.05
O-2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	534	5.9	1.91
O-2,6- <i>i</i> Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	1370	5.7	2.05
O-2,6- <i>i</i> Pr <sub>2</sub> -4- <i>t</i> BuC <sub>6</sub> H <sub>2</sub>	2680	5.2	2.18
O-2,6- <i>t</i> Bu <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	258	5.1	2.01
O-2,6- <i>t</i> Bu <sub>2</sub> -4-MeC <sub>6</sub> H <sub>2</sub>	54	4.6	1.98
N=C <sup><i>t</i></sup> Bu <sub>2</sub> <sup>d</sup>	8	10.6	1.9

Syndiotactic polystyrene as acetone insoluble fraction.

<sup>a</sup> Conditions: catalyst 1.0  $\mu\text{mol}$ , styrene/toluene = 5/9 mL, MAO 3.0 mmol (Al/Ti = 3000), 10 min at 25 °C.

<sup>b</sup> Activity in kg *s*-PS/mol Ti h.

<sup>c</sup> GPC data in THF vs. polystyrene standards.

<sup>d</sup> Ti 10.0  $\mu\text{mol}$ , styrene/toluene = 1/10 mL, 30 min.

Table 22

Ethylene/1-hexene copolymerization of by Cp\*TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**1a**)– and [Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(N<sup>*t*</sup>Bu)]TiCl<sub>2</sub> (**16**)–MAO catalyst systems [36]<sup>a</sup>

Complex (μmol)	Ethylene (atm)	1-Hexene (conc.) <sup>b</sup>	Activity <sup>c</sup> (×10 <sup>-3</sup> )	1-Hexene <sup>d</sup> (mol%)	M <sub>w</sub> <sup>e</sup> (×10 <sup>-5</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>f</sup>
<b>1a</b> (0.07)	5	1.45	179	43.5	3.17	1.77
<b>1a</b> (0.08)	5	0.73	83.2	28.7	3.82	1.80
<b>1a</b> (0.07)	7	1.45	263	38.0	3.37	1.87
<b>1a</b> (0.10)	7	1.09	120	36.0	3.34	1.73
<b>1a</b> (0.08)	7	0.73	103	24.6	4.55	1.98
<b>16</b> (0.65)	5	1.45	5.01	60.0	4.05	1.77
<b>16</b> (0.60)	5	0.73	9.49	30.0	7.45	2.05
<b>16</b> (0.65)	7	1.45	6.96	39.4	8.80	2.21
<b>16</b> (0.60)	7	0.73	14.6	23.7	11.9	2.30

<sup>a</sup> Reaction conditions: toluene + 1-hexene total 55 mL, MAO white solid (prepared by removing toluene and AlMe<sub>3</sub>) 2.00–3.00 mmol (by **1a**) or 2.75–3.25 mmol (by **16**), 4–6 min, 40 °C, 100 mL scale autoclave.

<sup>b</sup> 1-Hexene concentration, mmol/mL.

<sup>c</sup> Activity in kg polymer/mol Ti h.

<sup>d</sup> 1-Hexene content in copolymer estimated by <sup>13</sup>C NMR spectra.

<sup>e</sup> GPC data in *o*-dichlorobenzene vs. polystyrene standards.

ligands towards both the activity and the molecular weight is also present in this systems. Although the origin for this effect might not be perfectly clear at this moment, these facts do not deny the possibility that a neutral Ti(III) or a cationic Ti(IV) species also plays a role for this polymerization with this unique catalyst system, as described below.

### 3. Some ethylene copolymerizations by nonbridged half-titanocenes

#### 3.1. Ethylene/α-olefin copolymerization

Cp\*TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**1a**) exhibited a remarkable catalytic activity for ethylene/1-hexene copolymerization under optimal conditions, and that the activity was much higher than [Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(N<sup>*t*</sup>Bu)]TiCl<sub>2</sub> (CGC, **16**) in the presence of MAO (Table 22) [36]. The resultant copolymers by **1a**, possessed relatively high 1-hexene contents (24.6–43.5 mol%) that were of the same level as those obtained by CGC [36]. The M<sub>w</sub> values for resultant copolymers prepared by **1a** (M<sub>w</sub> = 3.17–4.55 × 10<sup>5</sup>) were lower than those prepared by CGC (M<sub>w</sub> = 4.05–11.9 × 10<sup>5</sup>), but possessed relatively high

molecular weights, unimodal molecular weight distributions (M<sub>w</sub>/M<sub>n</sub> = 1.77–1.98). Table 23 summarizes triad sequence distributions (monomer sequences) and dyads in the resultant copolymers estimated by <sup>13</sup>C NMR spectra [100]. It is clear that the percentages for HHE + EHH as well as HH sequences in the copolymers by **1a** were lower than those by **16**; r<sub>E</sub> · r<sub>H</sub> values by **1a** were 0.29–0.31, indicating that the copolymerization does not proceed in a random manner (comonomer incorporations does not proceed in a random manner). Generally, the copolymerization by ordinary metallocenes, linked half-titanocenes like CGC proceed in a random manner, as exemplified by CGC (r<sub>E</sub> × r<sub>H</sub> = 0.96–1.01, Table 23), and we thus assumed that the fact presented here by **1a** should be one of the unique characteristics for using nonbridged half-titanocenes in ethylene copolymerizations.

As shown in Table 24, the 1-hexene content in the resultant copolymer prepared by Cp'TiCl<sub>2</sub>O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [Cp' = Cp\* (**1a**), <sup>*t*</sup>Bu<sub>2</sub>C<sub>5</sub>H<sub>3</sub> (**17**), <sup>*t*</sup>BuC<sub>5</sub>H<sub>4</sub> (**18**)] depended upon the Cp' employed [36]. The <sup>*t*</sup>BuCp analogue (**18**) exhibited the highest level of 1-hexene incorporation among these complexes, indicating that the nature of Cp' affects the relative rate of monomer coordination or insertion. Triad sequence distributions

Table 23

Monomer sequence distribution of poly(ethylene-*co*-1-hexene)s prepared by Cp\*TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**1a**)– and [Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(N<sup>*t*</sup>Bu)]TiCl<sub>2</sub> (**16**)–MAO catalyst systems [36]<sup>a</sup>

Complex	Ethylene (atm)	1-Hexene (conc. <sup>b</sup> )	1-Hexene <sup>c</sup> (mol%)	Triad sequence distribution <sup>d</sup> (%)						Dyads <sup>e</sup>			r <sub>E</sub> · r <sub>H</sub> <sup>f</sup>
				EEE	EEH + HEE	HEH	EHE	HHE + EHH	HHH	EE	EH + HE	HH	
<b>1a</b>	7	1.45	38.0	17.3	30.4	14.3	22.5	14.0	1.5	32.4	59.0	8.5	0.31
<b>1a</b>	5	0.73	28.7	31.1	31.3	8.9	21.5	6.8	0.4	46.8	49.5	3.7	0.29
<b>1a</b>	7	0.73	24.6	40.0	29.6	5.8	19.4	4.6	0.6	55.1	42.5	2.4	0.29
<b>16</b>	7	1.45	39.4	23.3	28.6	8.7	14.3	20.0	5.1	37.6	47.4	15.0	1.01
<b>16</b>	5	0.73	30.0	35.5	28.6	5.9	14.2	14.4	1.4	49.8	41.6	8.6	0.99
<b>16</b>	7	0.73	23.7	45.3	27.2	3.8	13.8	9.4	0.5	58.9	35.9	5.2	0.96

<sup>a</sup> Detailed polymerization conditions, see Table 22.

<sup>b</sup> Initial 1-hexene concentration (mmol/mL).

<sup>c</sup> 1-Hexene content in copolymer determined by <sup>13</sup>C NMR spectra.

<sup>d</sup> Calculated by <sup>13</sup>C NMR spectra.

<sup>e</sup> [EE] = [EEE] + 1/2[EEH + HEE], [EH] = [HEH] + [EHE] + 1/2{[EEH + HEE] + [HHE + EHH]}, [HH] = [HHH] + 1/2[HHE + EHH].

<sup>f</sup> r<sub>E</sub> × r<sub>H</sub> = 4[EE][HH]/[EH + HE]<sup>2</sup>.

Table 24

Ethylene/1-hexene copolymerization by Cp'TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and [Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(N<sup>t</sup>Bu)]TiCl<sub>2</sub> (**16**)–MAO catalyst systems [Cp' = Cp\* (**1a**), 1,3-*i*-Bu<sub>2</sub>C<sub>5</sub>H<sub>3</sub> (**17**), and <sup>t</sup>BuC<sub>5</sub>H<sub>4</sub> (**18**)] [36]<sup>a</sup>

Complex (μmol)	Al/Ti <sup>b</sup> (×10 <sup>-3</sup> )	Ethylene (atm)	1-Hexene (conc. <sup>c</sup> )	Activity <sup>d</sup>	1-Hexene <sup>e</sup> (mol%)	M <sub>w</sub> <sup>f</sup> (×10 <sup>-5</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>f</sup>
<b>1a</b> (0.08)	25	5	0.73	83,200	28.7	3.82	1.80
<b>16</b> (0.60)	5.0	5	0.73	9,490	30.0	7.45	2.05
<b>17</b> (0.30)	9.0	5	0.73	11,300	27.1	1.97	1.82
<b>18</b> (0.60)	5.0	5	0.73	6,410	32.0	1.14	1.99
<b>1a</b> (0.08)	25	7	0.73	10,300	24.6	4.55	1.98
<b>17</b> (0.45)	6.5	7	1.45	6,850	33.9	1.24	1.78
<b>18</b> (0.60)	3.3	7	0.73	14,200	26.9	1.27	1.60

<sup>a</sup> Reaction conditions: toluene + 1-hexene, total 55 mL, MAO white solid (prepared by removing toluene and AlMe<sub>3</sub>), time, 5–8 min, 100 mL scale autoclave.

<sup>b</sup> Molar ratio of Al/Ti.

<sup>c</sup> 1-Hexene concentration mmol/mL.

<sup>d</sup> Activity in kg polymer/mol Ti h.

<sup>e</sup> 1-Hexene content in copolymer estimated by <sup>13</sup>C NMR spectra.

<sup>f</sup> GPC in *o*-dichlorobenzene vs polystyrene standard.

(monomer sequences) in the resultant copolymers estimated by <sup>13</sup>C NMR spectra [98], and the monomer reactivity ratios [101] are summarized in Table 25. The distributions showed that the contents of EHE and HHE + EHH sequences and the resultant  $r_E \times r_H$  values ( $r_E$  and  $r_H$  are the monomer reactivity ratios of ethylene and 1-hexene, respectively) by **1a**, **17**, **18** are significantly different from that by CGC (**16**) under the same conditions. The monomer reactivity ratios by CGC are consistent with those reported previously [4,15], and the values was larger than those obtained by **1a**, **18**. Moreover,  $r_E$ ,  $r_H$ , and  $r_E \cdot r_H$  values by **1a** were not strongly affected either by the reaction temperature or by the Al/Ti molar ratio under the present conditions ( $r_E \times r_H = 0.28\text{--}0.32$ ,  $r_E = 2.29\text{--}2.70$ ,  $r_H = 0.11\text{--}0.13$ , 15–50 °C and Al/Ti = 30,000–50,000) [36b]. Also noteworthy is that the sequence distributions as well as their  $r_E$ ,  $r_H$ , values in the copolymerizations were strongly affected by the substituent on Cp'. These observations are significantly different from those observed in copolymerizations by ordinary metallocene catalysts, and we thus assume that these are one of the unique characteristics for using nonbridged half-titanocenes for olefin (co)polymerizations.

### 3.2. Copolymerization of ethylene with styrene

It has been well known that ethylene/styrene copolymerization by ordinary half-sandwich complex such as Cp'TiX<sub>3</sub> (X = Cl, OMe, CH<sub>2</sub>Ph, etc.) afforded a mixture of polyethylene, syndiotactic polystyrene and poly(ethylene-*co*-styrene) [102]. Moreover, the observed activities were low and both the selectivity of product and the activity were highly depended upon cocatalyst used as well as pretreatment conditions (Scheme 3). The facts were believed to be due to that the active species between ethylene and styrene polymerizations are different. In contrast, the copolymerization by [Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(N<sup>t</sup>Bu)]TiCl<sub>2</sub> (CGC) afforded poly(ethylene-*co*-styrene) exclusively, but styrene head-to-tail repeat units were not observed and synthesis of the copolymer with high styrene contents was thus seemed difficult [103].

In contrast, we reported recently that the ethylene/styrene copolymerization by (aryloxo)(cyclopentadienyl)titanium complexes took place efficiently, affording poly(ethylene-*co*-styrene)s exclusively without by-producing polyethylene and/or syndiotactic polystyrene (Scheme 22), and these complexes

Table 25

Selected monomer sequence distributions of poly(ethylene-*co*-1-hexene)s prepared by Cp'TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [Cp' = Cp\* (**1a**), 1,3-*i*-Bu<sub>2</sub>C<sub>5</sub>H<sub>3</sub> (**17**), <sup>t</sup>BuC<sub>5</sub>H<sub>4</sub> (**18**)] and [Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(N<sup>t</sup>Bu)]TiCl<sub>2</sub> (**16**)–MAO catalyst systems [36]<sup>a</sup>

Cat.	1-Hexene <sup>b</sup> (mol%)	Triad sequence distribution <sup>c</sup> (%)						Dyad <sup>d</sup>			$r_E \cdot r_H^e$	$r_E^f$	$r_H^f$
		EEE	EEH + HEE	HEH	EHE	HHE + EHH	HHH	EE	EH + HE	HH			
<b>1a</b>	28.7	31.1	31.3	8.9	21.5	6.8	0.4	46.8	49.5	3.7	0.28	2.70	0.10
<b>1a</b>	24.6	40.0	29.6	5.8	19.4	4.6	0.6	55.1	42.5	2.4	0.29	2.64	0.11
<b>17</b>	33.9	26.0	29.7	10.4	20.5	12.0	1.4	40.9	51.7	7.4	0.45	3.23	0.14
<b>17</b>	27.1	34.6	31.2	7.1	18.4	7.8	0.9	50.3	45.0	4.8	0.48	3.19	0.15
<b>18</b>	32.0	27.6	31.4	9.0	20.1	10.9	1.0	43.3	50.2	6.5	0.45	2.46	0.18
<b>18</b>	26.9	35.9	31.1	6.2	19.2	7.3	0.4	51.4	44.6	4.0	0.41	2.35	0.18
<b>16</b>	30.0	35.5	28.6	5.9	14.2	14.4	1.4	49.8	41.6	8.6	0.99	3.42	0.29

<sup>a</sup> For detailed polymerization conditions, see Table 24.

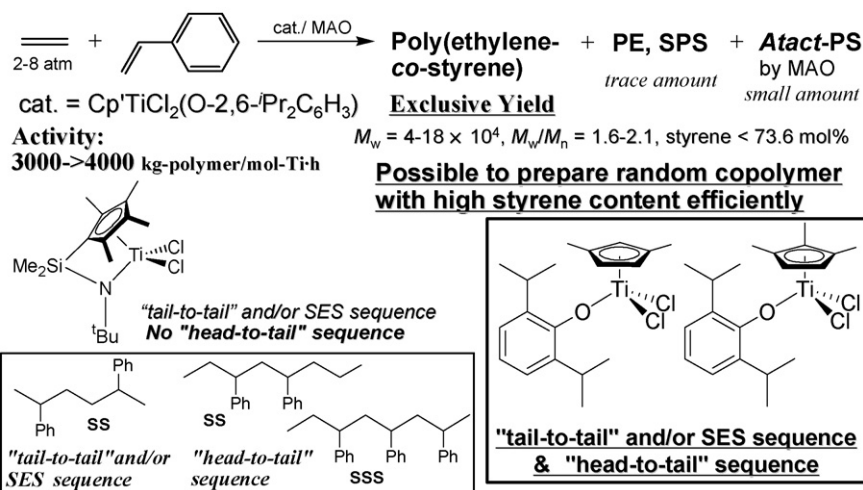
<sup>b</sup> 1-Hexene content in copolymer determined by <sup>13</sup>C NMR spectra.

<sup>c</sup> Determined by <sup>13</sup>C NMR spectra.

<sup>d</sup> [EE] = [EEE] + 1/2[EEH + HEE], [EH] = [HEH] + [EHE] + 1/2{[EEH + HEE] + [HHE + EHH]}, [HH] = [HHH] + 1/2[HHE + EHH].

<sup>e</sup>  $r_E \times r_H = 4[EE][HH]/[EH + HE]^2$ .

<sup>f</sup>  $r_E = [H]_0/[E]_0 \times 2[EE]/[EH + HE]$ ,  $r_H = [E]_0/[H]_0 \times 2[HH]/[EH + HE]$ , [E]<sub>0</sub> and [H]<sub>0</sub> are the initial monomer concentrations.

Ethylene/styrene copolymerization by  $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ 

Scheme 22. Copolymerization of ethylene with styrene catalyzed by  $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ -MAO catalyst systems: exclusive synthesis of poly(ethylene-co-styrene)s with high styrene contents in a random manner [37].

showed more efficient styrene incorporation than CGC. (Table 26) [35a,37]. The resultant copolymers possessed relatively high molecular weights with unimodal molecular weight distributions, and the copolymers possessed a single composition confirmed by sole  $T_g$  peaks in the DSC thermograms, cross fractionation chromatography (CFC), and by GPC attached with FT-IR (GPC/FT-IR) [37]. Fig. 3 shows typical  $^{13}\text{C}$  NMR spectra (methylene and methine region) of the copolymers (THF soluble fraction) prepared by  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$  (left) or  $(1,3\text{-Me}_2\text{C}_5\text{H}_3)\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  (right)-MAO catalyst systems (methylene and methine region, THF soluble fraction). In addition to the resonances at  $\delta = 34.3$  and  $35.1$  ppm, which are attributed to  $S_{\alpha\beta}$  (tail-to-tail coupling of styrene unit or head-to-head bridged by an intervening ethylene unit, SES), the resonances at  $\delta = 40.7\text{--}41.0$  ppm ( $T_{\beta\beta}$ , three styrene unit connected to head-to-tail coupling) and  $43.1\text{--}45$  ppm ( $S_{\alpha\alpha}$  and  $T_{\beta\delta}$ , two styrene unit connected to head-to-tail coupling) were observed [37]. This is an especially interesting contrast

with that prepared by  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$  based catalyst. The styrene content in the copolymer increased upon increasing the initial styrene concentration in the reaction mixture, and in one case, the styrene content up to 73.6 mol% could be thus attained, and the substituent on cyclopentadienyl group affected the catalytic activity, styrene incorporation, and regioselectivity of styrene insertion [37]. It was thus concluded that  $\text{Cp}^*\text{TiCl}_2(\text{OAr})$  exhibited unique characteristics for copolymerization of ethylene with styrene, affording poly(ethylene-co-styrene)s exclusively.

Ethylene/styrene copolymerization by  $\text{Cp}^*\text{TiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$  took place in a living manner in the presence of MAO cocatalyst, although the homopolymerization of ethylene nor styrene did not proceed in a living manner [51c]. Both cyclopentadienyl fragment ( $\text{Cp}^*$ ) and anionic donor ligand (L) in  $\text{Cp}^*\text{TiCl}_2(\text{L})$  directly affect toward the copolymerization behavior, the catalytic activities as well as the styrene incorporation; only the above set showed the living copolymerization [51d]. No styrene repeating

Table 26

Ethylene/styrene copolymerization by  $\text{Cp}^*\text{TiCl}_2(\text{OAr})$  ( $\text{Cp}^* = 1,3\text{-Me}_2\text{C}_5\text{H}_3$ ,  $1,2,3\text{-Me}_3\text{C}_5\text{H}_2$ ;  $\text{OAr} = \text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ) or  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ -MAO catalyst systems [37]<sup>a</sup>

Complexes	Styrene (mL)	Activity <sup>b</sup>	THF Soluble (E/S copolymer)			
			Content <sup>c</sup> (wt.%)	$M_w^d$ ( $\times 10^{-4}$ )	$M_w/M_n^d$	Styrene (mol%) <sup>e</sup>
$(1,3\text{-Me}_2\text{C}_5\text{H}_3)\text{TiCl}_2(\text{OAr})$	3	3670	97.1	6.4	1.8	32.3
$(1,3\text{-Me}_2\text{C}_5\text{H}_3)\text{TiCl}_2(\text{OAr})$	5	4280	98.2	6.0	2.1	38.5
$(1,3\text{-Me}_2\text{C}_5\text{H}_3)\text{TiCl}_2(\text{OAr})$	10	4140	98.2	3.7	1.6	49.0
$(1,2,3\text{-Me}_3\text{C}_5\text{H}_2)\text{TiCl}_2(\text{OAr})$	3	4100	99.1	17.0	1.6	26.0
$(1,2,3\text{-Me}_3\text{C}_5\text{H}_2)\text{TiCl}_2(\text{OAr})$	5	3070	98.3	11.0	1.7	38.8
$(1,2,3\text{-Me}_3\text{C}_5\text{H}_2)\text{TiCl}_2(\text{OAr})$	10	2720	97.8	6.6	1.6	51.2
$[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ (16)	10	5630	99.6	18.0	1.8	32.7

<sup>a</sup> Reaction conditions: catalyst 1.0  $\mu\text{mol}$  (2  $\mu\text{mol}/\text{mL}$  toluene), ethylene 4 atm, total volume of toluene and styrene = 30 mL, MAO white solid (Al/Ti = 2000, molar ratio), 25  $^\circ\text{C}$ , 10 min.

<sup>b</sup> Activity (kg polymer/mol Ti h), polymer yield in acetone insoluble fraction.

<sup>c</sup> Percentage of content in copolymer based on polymer obtained.

<sup>d</sup> GPC data in *o*-dichlorobenzene vs. polystyrene standard.

<sup>e</sup> Styrene content (mol%) in copolymer by  $^1\text{H}$  NMR ( $\text{C}_2\text{D}_2\text{Cl}_4$ ).

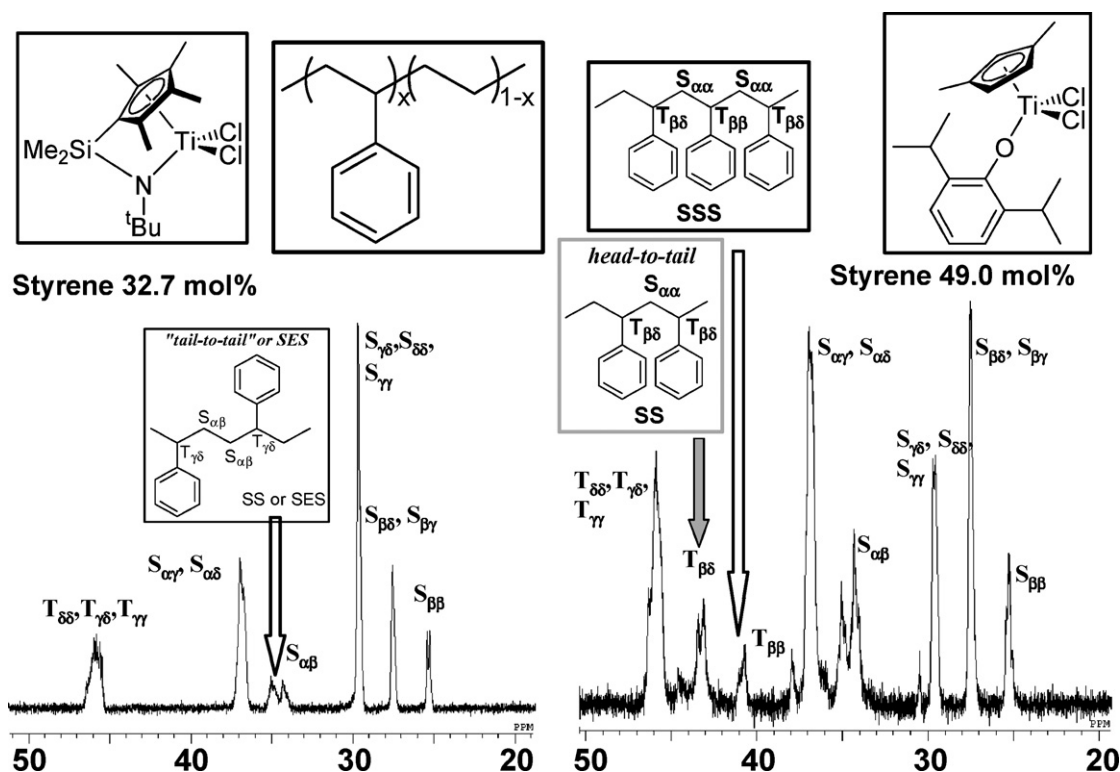


Fig. 3.  $^{13}\text{C}$  NMR spectra (in  $\text{CDCl}_3$  at  $60^\circ\text{C}$ ) of poly(ethylene-*co*-styrene)s prepared by  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$  (left) or  $(1,3\text{-Me}_2\text{C}_5\text{H}_3)\text{TiCl}_2(\text{O-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{-MAO}$  catalyst systems (methylene and methine region, THF soluble fraction).

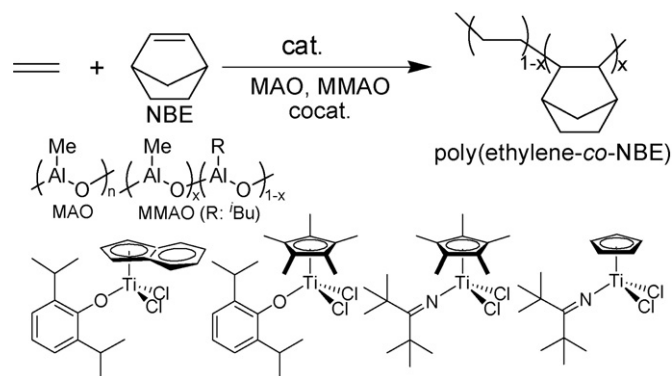
units were observed in the resultant poly(ethylene-*co*-styrene)s, assuming that a certain degree of the styrene insertion inhibit the degree of chain transfer in this catalysis.

### 3.3. Copolymerization of ethylene with cyclic olefin

Cyclic olefin copolymers (COC) like poly(ethylene-*co*-norbornene)s attract considerable attention as amorphous materials with a promising combination of high transparency in the UV–vis region and humidity as well as thermal resistance (high glass transition temperature,  $T_g$ ) [104]. It is known that both bridged zirconocenes and linked half-titanocenes showed high catalytic activities for ethylene/norbornene (NBE) copolymerization [38,105–108]. However, successful examples for the efficient synthesis of random, high molecular weight copolymers with high NBE contents (>50 mol%), which possess high  $T_g$  (>150  $^\circ\text{C}$ ), have been limited. This is not only because both the activity and molecular weights for the copolymer generally decrease upon increasing the NBE contents (as described below), but also because the microstructure in the copolymer possessed few NBE repeat units and contained alternating ethylene-NBE sequences in addition to the isolated NBE units due to the difficulty for repeated insertion of NBE.

$\text{CpTiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$  exhibits both remarkable catalytic activity and efficient norbornene (NBE) incorporation for ethylene/NBE copolymerization in the presence of MAO (activities 31,500–90,000 kg polymer/mol Ti h, ethylene 2 atm), affording poly(ethylene-*co*-NBE)s with both high molecular weights ( $M_n = 3.23\text{--}4.44 \times 10^5$ ,  $M_w/M_n = 2.00\text{--}2.09$ ) and high NBE con-

tents (58.8–73.5 mol%), and the activity increased at higher temperature. Both the activities and the NBE incorporations in the copolymerization by  $\text{Cp}'\text{TiCl}_2(\text{X})$  [ $\text{X} = \text{N}=\text{C}^t\text{Bu}_2$  and  $\text{Cp}' = \text{Cp}, \text{Cp}^*$ ;  $\text{X} = \text{O-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3$  and  $\text{Cp}' = \text{Cp}, \text{Cp}^*$  and indenyl] were highly influenced by both  $\text{Cp}'$  and  $\text{X}$  employed (Scheme 23), and the polymerization behaviors were different from ordinary metallocenes,  $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$  (Table 27) [109].  $^{13}\text{C}$  NMR spectra for poly(ethylene-*co*-NBE)s showed that resonances ascribed to NBE dyads were observed for the copolymers prepared by (indenyl) $\text{TiCl}_2(\text{O-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)$  and  $\text{CpTiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ , and the microstructures thus possessed a mixture of NBE repeat units (including dyads, triads) in addition to the alternating, isolated NBE sequences. The observed results are unique contrast with those prepared by ordi-



Scheme 23. Ethylene/norbornene copolymerization catalyzed by half-titanocenes [38,109].



Table 27

Copolymerization of ethylene with norbornene (NBE) by Cp'TiCl<sub>2</sub>(X) [X=O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and Cp'=indenyl, Cp\*; X=N=C'Bu<sub>2</sub> and Cp'=Cp\*, Cp], [Me<sub>2</sub>Si(indenyl)<sub>2</sub>]ZrCl<sub>2</sub>, [Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(N'Bu)]TiCl<sub>2</sub>-MAO catalyst systems [109]<sup>a</sup>

Complexes (μmol)	NBE concentration <sup>b</sup>	Activity <sup>c</sup>	M <sub>n</sub> <sup>d</sup> (× 10 <sup>-4</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>d</sup>	NBE <sup>e</sup> (mol%)
(Indenyl)TiCl <sub>2</sub> (O-2,6- <i>i</i> -Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) (0.2)	–	6960	22.5	1.88	–
(Indenyl)TiCl <sub>2</sub> (O-2,6- <i>i</i> -Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) (0.2)	0.2	10500	14.6	1.56	14.0
(Indenyl)TiCl <sub>2</sub> (O-2,6- <i>i</i> -Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) (0.5)	1.0	2300	5.9	1.82	35.2
Cp*TiCl <sub>2</sub> (O-2,6- <i>i</i> -Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) (0.2)	–	8400	65.2	1.90	–
Cp*TiCl <sub>2</sub> (O-2,6- <i>i</i> -Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) (0.2)	0.2	6540	57.9	1.61	8.2
Cp*TiCl <sub>2</sub> (O-2,6- <i>i</i> -Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ) (0.2)	1.0	2640	29.6	1.46	21.7
Cp*TiCl <sub>2</sub> (N=C'Bu <sub>2</sub> ) (0.05)	–	19680	42.2	2.45	–
Cp*TiCl <sub>2</sub> (N=C'Bu <sub>2</sub> ) (0.05)	0.2	31700	52.3	2.47	12.7
Cp*TiCl <sub>2</sub> (N=C'Bu <sub>2</sub> ) (0.05)	1.0	22200	97.0	2.04	20.3
CpTiCl <sub>2</sub> (N=C'Bu <sub>2</sub> ) (0.1)	–	5880	45.2	2.30	–
CpTiCl <sub>2</sub> (N=C'Bu <sub>2</sub> ) (0.02)	0.2	21600	70.6	1.85	17.8
CpTiCl <sub>2</sub> (N=C'Bu <sub>2</sub> ) (0.02)	1.0	40200	71.9	2.92	40.7
[Me <sub>2</sub> Si(indenyl) <sub>2</sub> ]ZrCl <sub>2</sub> (0.10)	0.2	28860	23.1	2.02	10.8
[Me <sub>2</sub> Si(indenyl) <sub>2</sub> ]ZrCl <sub>2</sub> (0.10)	1.0	4860	22.9	2.37	29.5
[Me <sub>2</sub> Si(C <sub>5</sub> Me <sub>4</sub> )(N'Bu)]TiCl <sub>2</sub> (0.50)	0.2	2460	21.1	1.88	9.6
[Me <sub>2</sub> Si(C <sub>5</sub> Me <sub>4</sub> )(N'Bu)]TiCl <sub>2</sub> (0.50)	1.0	2000	12.8	2.15	26.5

<sup>a</sup> Conditions: toluene + NBE total 50 mL, ethylene 4 atm, 25 °C, 10 min, MAO white solid (prepared by removing AlMe<sub>3</sub>, toluene from PMAO) 3.0 mmol.

<sup>b</sup> NBE concentration charged (mmol/mL).

<sup>c</sup> Activity in kg polymer/mol Ti h.

<sup>d</sup> GPC data in *o*-dichlorobenzene vs. polystyrene standards.

<sup>e</sup> NBE content (mol%) estimated by <sup>13</sup>C NMR spectra.

nary metallocenes as well as by [Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(N'Bu)]TiCl<sub>2</sub>, and this may be suited as an appropriate explanation for observed difference in the NBE incorporation.

Cyclohexene (CHE) has been incorporated into the polymer chain in ethylene/CHE copolymerization by Cp'TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)-MAO catalysts [39]. Effect of substituent in cyclopentadienyl fragment was found to be very important for the CHE incorporation; both the *tert*-BuCp and 1,2,4-Me<sub>3</sub>Cp analogues showed the efficient CHE incorporation whereas negligible amount of CHE incorporation was observed by both the indenyl, the Cp\* analogue under the same conditions. Cp-ketimide analogue, CpTiCl<sub>2</sub>(N=C'Bu<sub>2</sub>), zirconocene like Cp<sub>2</sub>ZrCl<sub>2</sub>, linked half-titanocene like [Me<sub>2</sub>Si(C<sub>5</sub>Me<sub>4</sub>)(N'Bu)]TiCl<sub>2</sub> did not show any CHE incorporations under the

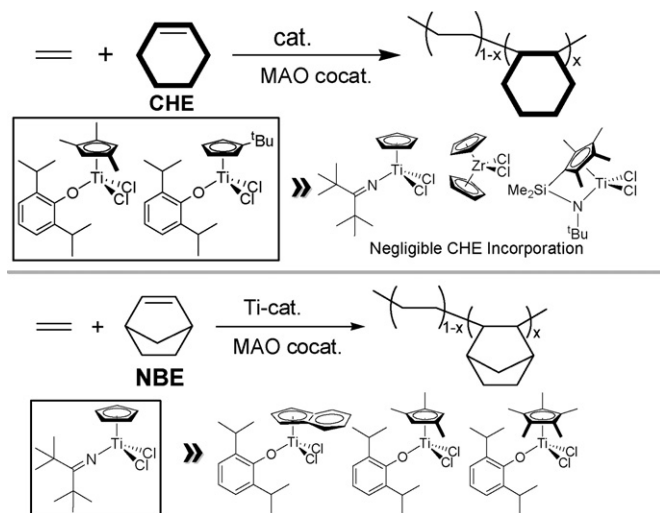
same conditions, unique characteristics for using this type of catalyst precursor for the present copolymerization have thus been emphasized. Unique contrast that effective catalyst precursor (ligand set) for ethylene/norbornene copolymerization was different from that for ethylene/CHE copolymerization (Scheme 24). Although the exact reason is not clear at this moment, we believe that coordination energy into the cationic species may influence the efficient comonomer incorporation as seen in the ethylene/norbornene copolymerization [38b,109].

#### 4. Summary and outlook

As introduced above, *nonbridged* half-metallocenes containing anionic donor ligand of the type, Cp'(L)MX<sub>2</sub>, displayed unique characteristics that are different from those especially by ordinary catalysts. Modifications of both the cyclopentadienyl fragment and anionic donor ligands (kind of anionic donor ligand, and the substituents) were thus very important for the success. We recently found that our original catalyst, Cp'TiCl<sub>2</sub>(OAr), produced new polyolefins that had not been prepared by the conventional catalysts. Since several interesting and important findings that should be very important from both academic and industrial viewpoints have been appeared, particular attention should be thus paid to explore the possibility for preparing precise polyolefin materials by using controlled polymerization technique.

#### Acknowledgements

Our research efforts were partly supported by Grant-in-Aid for Scientific Research (B) from the Japan Society for the Promotion of Science (JSPS, No. 1355253, No. 18350055), Kansai



Scheme 24. Effect of ligands between ethylene/cyclohexene [39] and ethylene/norbornene [109] copolymerizations.

Research Foundation for Technology Promotion (KRF), and The Japan Securities Scholarship Foundation (JSSF), SUZUKI Foundation, and by The Sumitomo Foundation for Basic Science Research (051082). K.N. would like to express his thanks to Tosoh Finechem Co. for donating MAO. J.L. and B.K. expresses their sincere thanks to JSPS for postdoctoral fellowships (P05397, P05157).

## References

- [1] H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1143.
- [2] W. Kaminsky, *Macromol. Chem. Phys.* 197 (1996) 3903.
- [3] W. Kaminsky, M. Arndt, *Adv. Polym. Sci.* 127 (1997) 143.
- [4] J. Suhm, J. Heinemann, C. Wörner, P. Müller, F. Stricker, J. Kressler, J. Okuda, R. Mülhaupt, *Macromol. Symp.* 129 (1998) 1.
- [5] A.L. McKnight, R.M. Waymouth, *Chem. Rev.* 98 (1998) 2587.
- [6] (a) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 429;  
(b) V.C. Gibson, S.K. Spitzmesser, *Chem. Rev.* 103 (2003) 283.
- [7] J.A. Gladysz (Ed.), *Frontiers in Metal-Catalyzed Polymerization (Special Issue)*. *Chem. Rev.* 100 (2000) 4;  
(a) S.D. Ittel, L.K. Johnson, M. Brookhart, *Chem. Rev.* 100 (2000) 1169;  
(b) H.G. Alt, A. Köppl, *Chem. Rev.* 100 (2000) 1205;  
(c) E.Y.-X. Chen, T.J. Marks, *Chem. Rev.* 100 (2000) 1391.
- [8] K. Nomura, in: L.P. Bevy (Ed.), *New Developments in Catalysis Research*, Nova Science Publishers, Inc., New York, USA, 2005, p. 199.
- [9] Progress in olefin polymerization catalysts and polyolefin materials, *Stud. Surf. Sci. Catal.*; T. Shiono, K. Nomura, M. Terano (Eds.), Special Symposium Issue on Asian Polyolefin Workshop 2005 (APO2005), vol. 161, Elsevier B.V., 2006; Nara, December 2005.
- [10] Influence of cyclopentadienyl-ring substituents in ethylene polymerization by substituted zirconocenes P.C. Möhring, N.J. Coville, *J. Organomet. Chem.* 479 (1994) 1.
- [11] For recent report, S.E. Reybuck, R.M. Waymouth, *Macromolecules* 37 (2004) 2342 (references related to this issue are cited therein).
- [12] (a) J.C.W. Chien, D.W. He, *J. Polym. Sci. Part A: Polym. Chem.* 29 (1991) 1585;  
(b) F.J. Karol, S.C. Kao, E.P. Wasserman, R.C. Brady, *New J. Chem.* 21 (1997) 797;  
(c) R. Kravchenko, R.M. Waymouth, *Macromolecules* 31 (1998) 1;  
(d) S.E. Reybuck, A. Meyer, R.M. Waymouth, *Macromolecules* 35 (2002) 637;  
(e) R. Quijada, J. Dupont, M.S.L. Miranda, R.B. Scipioni, G.B. Galland, *Macromol. Chem. Phys.* 196 (1995) 3991;  
(f) R. Quijada, R.B. Scipioni, R.S. Mauler, G.B. Galland, M.S.L. Miranda, *Polym. Bull. (Berlin)* 35 (1995) 299;  
(g) A. Zambelli, A. Grassi, M. Galimberti, R. Mazzocchi, F. Piemontesi, *Makromol. Chem. Rapid Commun.* 12 (1991) 523;  
(h) C. Lehtinen, B. Lofgren, *Eur. Polym. J.* 33 (1997) 115.
- [13] (a) For example, J.A.M. Canich, G.G. Hlatky, H.W. Turner, US Patent 542,236 (1990);  
(b) J.A.M. Canich (Exxon), US Patent 5,026,798 (1991);  
(c) J.A.M. Canich (Exxon), Eur. Patent Appl. 420436 (1991);  
(d) J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Rosen, G.W. Knight, S.-Y. Lai (Dow), Eur. Patent Appl. 416815 (1991);  
(e) J.C. Stevens, D.R. Neithamer (Dow), Eur. Patent Appl. 418022 (1991);  
(f) J. Okuda, F.J. Schattenmann, S. Wocadlo, W. Massa, *Organometallics* 14 (1995) 789;  
(g) K.L. du Plooy, U. Moll, S. Wocadlo, W. Massa, J. Okuda, *Organometallics* 14 (1995) 3129;  
(h) D.D. Devore, F.J. Timmers, D.L. Hasha, R.K. Rosen, T.J. Marks, P.A. Deck, C.L. Stern, *Organometallics* 14 (1995) 3132;  
(i) D.W. Carpenetti, L. Kloppenburg, J.T. Kupec, J.L. Petersen, *Organometallics* 15 (1996) 1572;  
(j) A.L. McKnight, M.A. Masood, R.M. Waymouth, *Organometallics* 16 (1997) 2879;  
(k) B.A. Harrington, D.J. Crowther, *J. Mol. Catal. A* 128 (1998) 79;  
(l) A.L. McKnight, R.M. Waymouth, *Macromolecules* 32 (1999) 2816.
- [14] (a) P.J. Shapiro, E. Bunel, W.P. Schaefer, J.E. Bercaw, *Organometallics* 9 (1990) 867;  
(b) P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, *J. Am. Chem. Soc.* 116 (1994) 4623.
- [15] J. Suhm, M.J. Schneider, R. Mülhaupt, *J. Mol. Catal. A* 128 (1998) 215.
- [16] J. Suhm, M.J. Schneider, R. Mülhaupt, *J. Polym. Sci. A* 35 (1997) 735.
- [17] K. Kunz, G. Erker, S. Döring, S. Bredeau, G. Kehr, R. Fröhlich, *Organometallics* 21 (2002) 1031.
- [18] K. Kunz, G. Erker, R. Fröhlich, H. Jacobsen, H. Berke, O. Blacque, *J. Am. Chem. Soc.* 124 (2002) 3316.  
Syntheses and ethylene (co)polymerization with cyclodimeric (sp<sup>2</sup>-C<sub>1</sub>)-bridged Cp/oxido group 4 metal complexes.
- [19] J. Hung, R.M. Waymouth, *J. Polym. Sci. Part A: Polym. Chem.* 43 (2005) 3840.
- [20] K. Nomura, N. Naga, M. Miki, K. Yanagi, A. Imai, *Organometallics* 17 (1998) 2152.
- [21] K. Nomura, N. Naga, M. Miki, K. Yanagi, *Macromolecules* 31 (1998) 7588.
- [22] (a) For example, K. Nomura, *Trend Organomet. Chem.* 4 (2002) 1;  
(b) K. Nomura, in: S.G. Pandalai (Ed.), *Recent Research Development in Polymer Science*, Transworld Research Network, Kerala, India, 2004, p. 105.
- [23] D.W. Stephan, *Organometallics* 24 (2005) 2548.
- [24] M.J. Ferreira, A.M. Martins, *Coord. Chem. Rev.* 250 (2006) 118.
- [25] Pioneering examples for chemistry in (R<sub>2</sub>N)<sub>2</sub>MX<sub>2</sub> related to olefin polymerisation: (a) J.A.M. Canich, H.W. Turner, WP 92/12162 (1992);  
(b) W.A. Herrmann, N.W. Huber, J. Behn, *Chem. Ber.* 125 (1992) 1405;  
(c) R.K. Minhas, L. Scoles, S. Wong, S. Gambarotta, *Organometallics* 15 (1996) 1113;  
(d) A.D. Horton, J. de With, *Chem. Commun.* (1996) 1375;  
(e) A.R. Johnson, W.M. Davis, C.C. Cummins, *Organometallics* 15 (1996) 3825.
- [26] Pioneering examples for chemistry in chelate group 4 bis(amide) complexes related to olefin polymerisation:  
(a) F.G.N. Cloke, T.J. Geldbach, P.B. Hitchcock, J.B. Love, *J. Organomet. Chem.* 506 (1996) 343;  
(b) K. Aoyagi, P.K. Gantzel, K. Kalai, T.D. Tilley, *Organometallics* 15 (1996) 923;  
(c) J.D. Scollard, D.H. McConville, J.J. Vittal, *Organometallics* 14 (1995) 5478;  
(d) T.H. Warren, R.R. Schrock, W.M. Davis, *Organometallics* 15 (1996) 562;  
(e) J.E. Bol, B. Hessen, J.H. Teuben, W.J.J. Smeets, A.L. Spek, *Organometallics* 11 (1992) 1981;  
(f) W.A. Herrmann, M. Denk, W. Scherer, F.R. Klingan, *J. Organomet. Chem.* 444 (1993) C21;  
(g) W.A. Herrmann, M. Denk, R.W. Albach, J. Behm, E. Herdweck, *Chem. Ber.* 124 (1991) 683;  
(h) V.H. Burger, D. Beiersdorf, *Z. Anorg. Allg. Chem.* 459 (1979) 111;  
(i) H. Burger, W. Geschwandtner, G.R. Lieward, *J. Organomet. Chem.* 259 (1983) 145;  
(j) J.D. Scollard, D.H. McConville, *J. Am. Chem. Soc.* 118 (1996) 10008;  
(k) J.D. Scollard, D.H. McConville, N.C. Payne, J.J. Vittal, *Macromolecules* 29 (1996) 5241;  
(l) S. Tinkler, R.J. Deeth, D.J. Duncalf, A. McCamley, *Chem. Commun.* (1996) 2623;  
(m) B. Tsuie, D.C. Swenson, R.F. Jordan, *Organometallics* 16 (1997) 1392;  
(n) F. Jäger, H.W. Roesky, H. Dorn, S. Shah, M. Noltemeyer, H.-G. Schmidt, *Chem. Ber.* 130 (1997) 399;  
(o) M. Oberthür, P. Arndt, R. Kempe, *Chem. Ber.* 129 (1997) 11087;  
(p) V.C. Gibson, B.S. Kimberley, A.J.P. White, D.J. Williams, P. Howard, *Chem. Commun.* (1998) 313;

- (q) L.T. Armistead, P.S. White, M.R. Gagné, *Organometallics* 17 (1998) 216;
- (r) T.H. Warren, R.R. Schrock, W.M. Davis, *Organometallics* 17 (1998) 308;
- (s) K. Nomura, N. Naga, K. Takaoki, A. Imai, *J. Mol. Catal. A* 130 (1998) L209;
- (t) K. Nomura, N. Naga, K. Takaoki, *Macromolecules* 31 (1998) 8009.
- [27] Pioneering examples for chemistry in chelate tridentate bis(amide) complexes related to olefin polymerisation;
- (a) A.D. Horton, J. de With, A.J. van der Linden, H. van der Weg, *Organometallics* 15 (1996) 2672;
- (b) F.G.N. Cloke, P.B. Hitchcock, J.B. Love, *J. Chem. Soc. Dalton Trans.* (1995) 25;
- (c) H.C.S. Clark, F.G.N. Cloke, P.B. Hitchcock, J.B. Love, A.P. Mainwright, *J. Organomet. Chem.* 501 (1995) 333;
- (d) R. Baumann, W.M. Davis, R.R. Schrock, *J. Am. Chem. Soc.* 119 (1997) 3830;
- (e) R.R. Schrock, F. Schattner, M. Aizenberg, W.M. Davis, *Chem. Commun.* (1998) 199.
- [28] For examples in syndiospecific styrene polymerization by  $Cp^*/TiX_3$ ;
- (a) N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules* 19 (1986) 2465;
- (b) N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules* 21 (1988) 3356;
- (c) T.H. Newman, R.E. Campbell, M.T. Malanga, *Metcon'93* 315 (1993);
- (d) N. Tomotsu, N. Ishihara, T.H. Newman, M.T. Malanga, *J. Mol. Catal. A* 128 (1998) 167;
- (e) N. Tomotsu, N. Ishihara, *Catal. Surv. Jpn.* 1 (1997) 89;
- (f) N. Tomotsu, *J. Synth. Org. Chem. Jpn.* 57 (1999) 450;
- (g) W. Kaminsky, S. Lenk, V. Scholz, H.W. Roesky, A. Herzog, *Macromolecules* 30 (1997) 7647;
- (h) J.C. Flores, J.C.W. Chien, M.D. Rausch, *Organometallics* 13 (1994) 4140;
- (i) J.C. Flores, J.C.W. Chien, M.D. Rausch, *Macromolecules* 29 (1996) 8030.
- [29] (a) S.W. Ewart, M. Baird, in: T.J. Marks, J.C. Stevens (Eds.), *Topics in Catalysis*, vol. 7, 1999, p. 1;
- (b) M.C. Baird, *Chem. Rev.* 100 (2000) 1471.
- [30] For example;
- (a) D.J. Gillis, M.-J. Tudoret, M.C. Baird, *J. Am. Chem. Soc.* 115 (1993) 2543;
- (b) R. Quyoum, Q. Wang, M.-J. Tudoret, M.C. Baird, *J. Am. Chem. Soc.* 116 (1994) 6435;
- (c) Q. Wang, R. Quyoum, D.J. Gillis, M.-J. Tudoret, D. Jeremic, B.K. Hunter, M.C. Baird, *Organometallics* 15 (1996) 693.
- [31] In this catalyst system with  $Cp^*TiMe_2(\mu-Me)B(C_6F_5)_3$  generated from  $Cp^*TiMe_3$  and  $B(C_6F_5)_3$ , styrene polymerization took place in both cationic (affording atactic polystyrene) and coordination insertion (affording syndiotactic styrene) manner. The cationic polymerization of isobutene also took place, and the 1-hexene polymerization afforded polymer with broad molecular weight distribution. Since the styrene homopolymerization also took place only with borate, MAO in a cationic manner, it might be difficult to estimate the catalytic activity with titanium catalyst.
- [32] One example was known for ethylene polymerization using the  $Cp^*Ti(O^iPr)Me_2-[HNEt_3]^+[B(C_6F_5)_4]^-$  system (4.08 kg of polymer/mol Ti, ethylene 1 atm, benzene, r.t. 20 min); J.C. Stevens, D.R. Neithamer, US Patent 5,064,802 (1991).
- [33] Report concerning ethylene polymerization using  $CpTiCl_2(O-4XC_6H_4)-Et_2AlCl$  (classical Ziegler type) catalyst system; W. Skupinski, A. Wasilewski, *J. Organomet. Chem.* 282 (1985) 69.
- [34] K. Nomura, T. Komatsu, Y. Imanishi, *J. Mol. Catal. A* 152 (2000) 249.
- [35] (a) K. Nomura, T. Komatsu, Y. Imanishi, *Macromolecules* 33 (2000) 8122;
- (b) D.-J. Byun, A. Fudo, A. Tanaka, M. Fujiki, K. Nomura, *Macromolecules* 37 (2004) 5520.
- [36] (a) K. Nomura, K. Oya, T. Komatsu, Y. Imanishi, *Macromolecules* 33 (2000) 3187;
- (b) K. Nomura, K. Oya, Y. Imanishi, *J. Mol. Catal. A* 174 (2001) 127.
- [37] K. Nomura, H. Okumura, K. Komatsu, N. Naga, *Macromolecules* 35 (2002) 5388.
- [38] (a) K. Nomura, M. Tsubota, M. Fujiki, *Macromolecules* 36 (2003) 3797;
- (b) W. Wang, T. Tanaka, M. Tsubota, M. Fujiki, S. Yamanaka, K. Nomura, *Adv. Synth. Catal.* 347 (2005) 433.
- [39] W. Wang, M. Fujiki, K. Nomura, *J. Am. Chem. Soc.* 127 (2005) 4582.
- [40] K. Nomura, K. Itagaki, M. Fujiki, *Macromolecules* 38 (2005) 2053.
- [41] K. Nomura, K. Itagaki, *Macromolecules* 38 (2005) 8121.
- [42] (a) K. Nomura, Y. Hatanaka, H. Okumura, M. Fujiki, K. Hasegawa, *Macromolecules* 37 (2004) 1693;
- (b) K. Nomura, A. Takemoto, Y. Hatanaka, H. Okumura, M. Fujiki, K. Hasegawa, *Macromolecules* 39 (2006) 4009.
- [43] A. Antiñolo, F. Carrillo-Hermosilla, A. Corrochano, J. Fernández-Baeza, A.R. Lara-Sanchez, M. Ribeiro, M. Lanfranchi, A. Otero, M.A. Pellinghelli, M.F. Portela, J.V. Santos, *Organometallics* 19 (2000) 2837.
- [44] S.A.A. Shah, H. Dorn, A. Voigt, H.W. Roesky, E. Parisini, H.-G. Schmidt, M. Noltemeyer, *Organometallics* 15 (1996) 3176.
- [45] K. Nomura, K. Fujii, *Organometallics* 21 (2002) 3042.
- [46] S. Doherty, R.J. Errington, A.P. Jarvis, S. Collins, W. Clegg, M.R.J. Elsegood, *Organometallics* 17 (1998) 3408.
- [47] (a) D.W. Stephan, J.C. Stewart, F. Guérin, R.E.v.H. Spence, W. Xu, D.G. Harrison, *Organometallics* 18 (1999) 1116;
- (b) D.W. Stephan, F. Guérin, R.E.v.H. Spence, L. Koch, X. Gao, S.J. Brown, J.W. Swabey, Q. Wang, W. Xu, P. Zoricak, D.G. Harrison, *Organometallics* 18 (1999) 2046;
- (c) N. Yue, E. Hollink, F. Guérin, D.W. Stephan, *Organometallics* 20 (2001) 4424;
- (d) D.W. Stephan, J.C. Stewart, F. Guérin, S. Courtenay, J. Kickham, E. Hollink, C. Beddie, A. Hoskin, T. Graham, P. Wei, R.E.V.H. Spence, W. Xu, L. Koch, X. Gao, D.G. Harrison, *Organometallics* 22 (2003) 1937;
- (e) E. Hollink, P. Wei, D.W. Stohan, *Organometallics* 23 (2004) 1562;
- (f) C. Beddie, E. Hollink, P. Wei, J. Gauld, D.W. Stephan, *Organometallics* 23 (2004) 5240.
- [48] D.W. Stephan, J. C. Stewart, S.J. Brown, J.W. Swabey, Q. Wang, EP881233 A1 (1998).
- [49] J. McMeeking, X. Gao, R.E.v.H. Spence, S.J. Brown, D. Jeremic, US Patent 6,114,481 (2000).
- [50] (a) S. Zhang, W.E. Piers, X. Gao, M. Parvez, *J. Am. Chem. Soc.* 122 (2000) 5499;
- (b) S. Zhang, W.E. Piers, *Organometallics* 20 (2001) 2088.
- [51] (a) K. Nomura, K. Fujita, M. Fujiki, *Catal. Commun.* 5 (2004) 413;
- (b) K. Nomura, K. Fujita, M. Fujiki, *J. Mol. Catal. A* 220 (2004) 133;
- (c) H. Zhang, K. Nomura, *J. Am. Chem. Soc.* 127 (2005) 9364;
- (d) H. Zhang, K. Nomura, *Macromolecules* 39 (2006) 5266.
- [52] (a) A.R. Dias, M.T. Duarte, A.C. Fernandes, S. Fernandes, M.M. Marques, A.M. Martins, J.F. da Silva, S.S. Rodrigues, *J. Organomet. Chem.* 689 (2004) 203;
- (b) A.M. Martins, M.M. Marques, J.R. Ascenso, A.R. Dias, M.T. Duarte, A.C. Fernandes, S. Fernandes, M.J. Ferreira, I. Matos, M.C. Oliveira, S.S. Rodrigues, C. Wilson, *J. Organomet. Chem.* 690 (2005) 874.
- [53] J. Richter, F.T. Edlmann, M. Noltemeyer, H.-G. Schmidt, M. Schmulinson, M.S. Eisen, *J. Mol. Catal. A* 130 (1998) 149.
- [54] R. Vollmerhaus, P. Shao, N.J. Taylor, S. Collins, *Organometallics* 18 (1999) 2731.
- [55] (a) K.C. Jayaratne, L.R. Sita, *J. Am. Chem. Soc.* 122 (2000) 958;
- (b) L.R. Sita, R. Babcock, *Organometallics* 17 (1998) 5228;
- (c) K.C. Jayaratne, R.J. Keaton, D.A. Henningsen, L.R. Sita, *J. Am. Chem. Soc.* 122 (2000) 10490;
- (d) R.J. Keaton, K.C. Jayaratne, D.A. Henningsen, L.A. Koterwas, L.R. Sita, *J. Am. Chem. Soc.* 123 (2001) 6197;
- (e) Y. Zhang, E.K. Reeder, R.J. Keaton, L.R. Sita, *Organometallics* 23 (2004) 3512.
- [56] W.P. Kretschmer, C. Dijkhuis, A. Meetsma, B. Hessen, J.H. Teuben, *Chem. Commun.* (2002) 608.
- [57] P.-J. Sinnema, T.P. Spaniol, J. Okuda, *J. Organomet. Chem.* 598 (2000) 179.
- [58] K. Nomura, K. Fujii, *Macromolecules* 36 (2003) 2633.

- [59] M.K. Mahanthappa, A.P. Cole, R.M. Waymouth, *Organometallics* 23 (2004) 836.
- [60] J. Huang, B. Lian, Y. Qian, W. Zhou, W. Chen, G. Zheng, *Macromolecules* 35 (2002) 4871.
- [61] R.K.J. Bott, D.L. Hughes, M. Schormann, M. Bochmann, S.J. Lancaster, *J. Organomet. Chem.* 665 (2003) 135.
- [62] V. Taberneria, T. Cuenca, E. Herdtweck, *J. Organomet. Chem.* 663 (2002) 173.
- [63] H. Ishino, S. Takemoto, K. Hirata, Y. Kanaizuka, M. Hidai, M. Nabika, Y. Seki, T. Miyatake, N. Suzuki, *Organometallics* 23 (2004) 454.
- [64] T. Yasumoto, T. Yamagata, K. Mashima, *Organometallics* 24 (2005) 3375.
- [65] N.L.S. Yue, D.W. Stephan, *Organometallics* 20 (2001) 2303.
- [66] C. Carraz, D.W. Stephan, *Organometallics* 19 (2000) 3791.
- [67] S.C. Cole, M.P. Coles, P.B. Hitchcock, *Organometallics* 24 (2005) 3279.
- [68] Q.H. Chen, J.L. Huang, J. Yu, *Inorg. Chem. Commun.* 8 (2005) 444.
- [69] A.P. Dove, X.J. Xie, R.M. Waymouth, *Chem. Commun.* (2005) 2152.
- [70] M. Tamm, S. Randoll, E. Herdtweck, N. Kleigrew, G. Kehr, G. Erker, B. Rieger, *Dalton Trans.* (2006) 459.
- [71] C.H. Qi, S.B. Zhang, J.H. Sun, *J. Organomet. Chem.* 690 (2005) 2941.
- [72] M.A. Esteruelas, A.M. López, A.C. Mateo, E. Oñate, *Organometallics* 25 (2006) 1448.
- [73] M. González-Maupoe, T. Cuenca, L.M. Frutos, O. Castaño, E. Herdtweck, *Organometallics* 22 (2003) 2694.
- [74] A.J. Nielson, J.A. Harrison, C.H. Shen, J.M. Waters, *Polyhedron* 25 (2006) 1729.
- [75] Y.L. Qian, H. Zhang, J.X. Zhou, W. Zhao, X.Q. Sun, J.L. Huang, *J. Mol. Catal. A* 208 (2004) 45.
- [76] Y. Perez, S. Morante-Zarcelo, I. Hierro, I. Sierra, I. Lopez-Solera, M. Monari, M. Fajardo, A. Otero, *J. Organomet. Chem.* 689 (2004) 3492.
- [77] K.S. Lee, Y. Kim, S.K. Ihm, Y. Do, S.W. Lee, *J. Organomet. Chem.* 691 (2006) 1121.
- [78] J. Chen, Z.J. Zheng, L. Pan, D. Pan, Y.S. Li, *J. Polym. Sci. Part A: Polym. Chem.* 43 (2005) 1562.
- [79] J. Chen, Y.S. Li, J.Q. Wu, N.H. Hu, *J. Mol. Catal. A* 232 (2005) 1.
- [80] J.R. Ascenso, A.R. Dias, J.A. Fernandes, A.M. Martins, S.S. Rodrigues, *Inorg. Chim. Acta* 356 (2003) 279.
- [81] K. Nomura, A. Tanaka, S. Katao, *J. Mol. Catal. A* 254 (2004) 197.
- [82] P. Gomez-Sal, A. Martin, M. Mena, P. Royo, R. Serrano, *J. Organomet. Chem.* 419 (1991) 77.
- [83] S.J. Sturla, S.L. Buchwald, *Organometallics* 21 (2001) 739.
- [84] (a) M.G. Thorn, J.S. Vilaro, P.E. Fanwick, I.P. Rothwell, *Chem. Commun.* (1998) 2427;  
(b) M.G. Thorn, J.S. Vilaro, J. Lee, B. Hanna, P.E. Fanwick, I.P. Rothwell, *Organometallics* 19 (2000) 5636.
- [85] K. Nomura, A. Fudo, *Inorg. Chim. Acta* 345 (2003) 37.  
The reaction of  $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-iPr}_2\text{C}_6\text{H}_3)$  (**1b**) with  $\text{B}(\text{C}_6\text{F}_5)_3$  in toluene- $d_8$  cleanly gave  $\text{Cp}^*\text{Ti}(\text{C}_6\text{F}_5)[\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2](\text{O}-2,6\text{-iPr}_2\text{C}_6\text{H}_3)$  upon stirring for long hours, unpublished results.
- [86] K. Nomura, A. Fudo, *J. Mol. Catal. A* 209 (2004) 9.
- [87] K. Nomura, K. Oya, Y. Imanishi, *Polymer* 41 (2000) 2755.
- [88] (a) S. Anfang, K. Harms, F. Weller, O. Borgmeier, H. Lueken, H. Schilder, K. Dehnicke, *Z. Anorg. Allg. Chem.* 624 (1998) 159;  
(b) T. Rubenstahl, F. Weller, S. Wacaldo, W. Massa, K. Dehnicke, *Z. Anorg. Allg. Chem.* 621 (1995) 953.
- [89] S. Arévalo, M.R. Bonillo, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, P. Gómez-Sal, P. Ortega, *J. Organomet. Chem.* 681 (2003) 228.
- [90] S. Arévalo, E. de Jesús, F.J. de la Mata, J.C. Flores, R. Gómez, *Organometallics* 20 (2001) 2583.
- [91] M.H. Lee, S.K. Kim, Y. Do, *Organometallics* 24 (2005) 3618.
- [92] D.-H. Kum, W. Jung, K. Kim, S.K. Noh, D.-H. Lee, W.S. Lyoo, *Polym. Chem. (Korea)* 30 (2006) 64.
- [93] A.E. Fenwick, K. Phomphrai, M.G. Thorn, J.S. Vilaro, C.A. Trefun, B. Hanna, P.E. Fanwick, I.P. Rothwell, *Organometallics* 23 (2004) 2146.
- [94] K. Phomphrai, A.E. Fenwick, S. Sharma, P.E. Fanwick, J.M. Caruthers, W.N. Delgass, M.M. Abu-Omar, I.P. Rothwell, *Organometallics* 25 (2006) 214.
- [95] (a) R.J. Keaton, K.C. Jayaratne, J.C. Fettinger, L.R. Sita, *J. Am. Chem. Soc.* 122 (2000) 12909;  
(b) K.C. Jayaratne, L.R. Sita, *J. Am. Chem. Soc.* 123 (2001) 10754;  
(c) Y. Zhang, R.J. Keaton, L.R. Sita, *J. Am. Chem. Soc.* 125 (2003) 9062;  
(d) Y. Zhang, L.R. Sita, *J. Am. Chem. Soc.* 126 (2004) 7776;  
(e) M.B. Harney, R.J. Keaton, J.C. Fettinger, L.R. Sita, *J. Am. Chem. Soc.* 128 (2006) 3420;  
(f) M.B. Harney, Y. Zhang, L.R. Sita, *Angew. Chem. Int. Ed.* 45 (2006) 2400.
- [96] Example for improvement in the catalytic activity (bimetallic catalyst system);  
N. Guo, L. Li, T.J. Marks, *J. Am. Chem. Soc.* 126 (2004) 6542.
- [97] K. Nomura, A. Fudo, *Catal. Commun.* 4 (2003) 269.
- [98] (a) S.W. Ewart, M.J. Sarsfield, D. Jeremic, T.L. Tremblay, E.F. Williams, M.C. Baird, *Organometallics* 17 (1998) 1502;  
(b) F. Barsan, M.C. Baird, *J. Chem. Soc. Chem. Commun.* (1995) 1065.
- [99] Examples for a mechanistic study concerning both styrene polymerization (and propylene/styrene copolymerization);  
(a) A. Grassi, A. Zambelli, F. Laschi, *Organometallics* 15 (1996) 480;  
(b) G. Minieri, P. Corradini, G. Guerra, A. Zambelli, L. Cavallo, *Macromolecules* 34 (2001) 5379;  
(c) M.K. Mahanthappa, R.M. Waymouth, *J. Am. Chem. Soc.* 123 (2001) 12093.
- [100] These calculations were made by the  $^{13}\text{C}$ -NMR spectra of copolymers;  
J.C. Randall, *JMS Rev. Macromol. Chem. Phys.* C29 (2/3) (1989) 201.
- [101] The calculation of  $r_E$  and  $r_H$  values are based on dyads and the initial monomer concentrations. Ethylene concentrations under the reaction conditions were estimated by the equation quoted by Kissin (Y.V. Kissin, *Isospecific Polymerization of Olefin with Heterogeneous Ziegler–Natta Catalysts*, Springer-Verlag, New York, 1985, p. 3.), and the ethylene solubilities in the reaction mixture (1 atm) were used as those in toluene reported in the following article;  
A. Sahgal, H.M. La, W. Hayduk, *Can. J. Chem. Eng.* 56 (1978) 354.
- [102] (a) P. Longo, A. Grassi, L. Oliva, *Makromol. Chem.* 191 (1990) 2387;  
(b) S. Naganuma, M. Kuramoto, *JP (Kokai) H3-7705* (1991) (Idemitsu Kosan Co.);  
(c) S. Naganuma, T. Tasaki, S. Machida, *JP (Kokai) H4-130114* (1992) (Idemitsu Kosan Co.);  
(d) P. Aaltonen, J. Seppälä, *Eur. Polym. J.* 30 (1994) 683;  
(e) C. Pellicchia, D. Pappalardo, M. D'Arco, A. Zambelli, *Macromolecules* 29 (1996) 1158;  
(f) L. Oliva, S. Mazza, P. Longo, *Macromol. Chem. Phys.* 197 (1996) 3115;  
(g) L. Oliva, L. Izzo, P. Longo, *Macromol. Rapid Commun.* 17 (1996) 745;  
(h) G. Xu, S. Lin, *Macromolecules* 30 (1997) 685;  
(i) D.-H. Lee, K.-B. Yoon, H.-Y. Kim, S.-S. Woo, S.K. Noh, *J. Appl. Polym. Sci.* 67 (1998) 2187;  
(j) Q. Wu, Z. Ye, Q. Gao, S. Lin, *Macromol. Chem. Phys.* 19 (1998) 1715.
- [103] (a) J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Rosen, G.W. Knight, S. Lai, *Eur. Patent Appl.* 416815 (1991) (Dow Chemical Co. Ltd.) (1992);  
(b) F.G. Sernetz, R. Mülhaupt, R.M. Waymouth, *Macromol. Chem. Phys.* 29 (1996) 1158;  
(c) F.G. Sernetz, R. Mülhaupt, F. Amor, T. Eberle, J. Okuda, *J. Polym. Sci. Part A: Polym. Chem.* 35 (1997) 1571;  
(d) G. Xu, *Macromolecules* 31 (1998) 2395;  
(e) F.G. Sernetz, R. Mülhaupt, *J. Polym. Sci. Part A: Polym. Chem.* 35 (1997) 2549;  
(f) R.E. Campbell, M.H. Mcadon, P.N. Nickias, J.T. Patton, O.D. Redwine, F.J. Timmers, *WO 98/09999* (1998) (The Dow Chemical Co.);  
(g) T. Arai, T. Ohtsu, S. Suzuki, *Macromol. Rapid Commun.* 19 (1998) 327.
- [104] (a) W. Kaminsky, *Adv. Catal.* 46 (2001) 89;  
(b) W. Kaminsky, I. Beulich, M. Arndt-Rosenau, *Macromol. Symp.* 173 (2001) 211;  
(c) H. Cherdron, M.-J. Brekner, F. Osan, *Angew. Makromol. Chem.* 223 (1994) 121.
- [105] (a) D. Ruchatz, G. Fink, *Macromolecules* 31 (1998) 4669;  
(b) D. Ruchatz, G. Fink, *Macromolecules* 31 (1998) 4674;

- (c) D. Ruchatz, G. Fink, *Macromolecules* 31 (1998) 4681;  
(d) D. Ruchatz, G. Fink, *Macromolecules* 31 (1998) 4684;  
(e) R.A. Wendt, G. Fink, *Macromol. Chem. Phys.* 202 (2001) 3490;  
(f) R.A. Wendt, G. Fink, *J. Mol. Catal. A* 203 (2003) 101.
- [106] (a) A. Provasoli, D.R. Ferro, I. Tritto, L. Boggioni, *Macromolecules* 32 (1999) 6697;  
(b) I. Tritto, C. Marestin, L. Boggioni, L. Zetta, A. Provasoli, D.R. Ferro, *Macromolecules* 33 (2000) 8931;  
(c) I. Tritto, C. Marestin, L. Boggioni, M.C. Sacchi, H.H. Brintzinger, D.R. Ferro, *Macromolecules* 34 (2001) 5770;  
(d) J. Forsyth, J.M. Pereña, R. Benavente, E. Pérez, I. Tritto, L. Boggioni, H.H. Brintzinger, *Macromol. Chem. Phys.* 202 (2001) 614;  
(e) I. Tritto, L. Boggioni, J.C. Jansen, K. Thorshaug, M.C. Sacchi, D.R. Ferro, *Macromolecules* 35 (2002) 616;  
(f) K. Thorshaug, R. Mendichi, L. Boggioni, I. Tritto, S. Trinkle, C. Friedrich, R. Mulhaupt, *Macromolecules* 35 (2002) 2903;  
(g) I. Tritto, L. Boggioni, D.R. Ferro, *Macromolecules* 37 (2004) 9681.
- [107] (a) B.A. Harrington, D.J. Crowther, *J. Mol. Catal. A* 128 (1998) 79;  
(b) A.L. McKnight, R.M. Waymouth, *Macromolecules* 32 (1999) 2816;  
(c) T. Hasan, T. Ikeda, T. Shiono, *Macromolecules* 37 (2004) 8503.
- [108] (a) P. Altamura, A. Grassi, *Macromolecules* 34 (2001) 9197;  
(b) Y. Yoshida, J. Saito, M. Mitani, Y. Takagi, S. Matsui, S. Ishii, T. Nakano, N. Kashiwa, T. Fujita, *Chem. Commun.* (2002) 1298;  
(c) J. Kiesewetter, W. Kaminsky, *Chem. Eur. J.* 9 (2003) 1750;  
(d) Y. Yoshida, J. Mohri, S. Ishii, M. Mitani, J. Saito, S. Matsui, H. Makio, T. Nakano, H. Tanaka, M. Onda, Y. Yamamoto, A. Mizuno, T. Fujita, *J. Am. Chem. Soc.* 126 (2004) 12023;  
(e) X.-F. Li, K. Dai, W.-P. Ye, L. Pan, Y.-S. Li, *Organometallics* 23 (2004) 1223.
- [109] K. Nomura, W. Wang, M. Fujiki, J. Liu, *Chem. Commun.* (2006) 2659.