

This article is published as part of the *Dalton Transactions* themed issue entitled:

d^0 organometallics in catalysis

Guest Editors John Arnold (UC Berkeley) and Peter Scott (University of Warwick)

Published in [issue 30, 2011](#) of *Dalton Transactions*



Image reproduced with permission of Guo-Xin Jin

Articles in the issue include:

PERSPECTIVES:

[Half-titanocenes for precise olefin polymerisation: effects of ligand substituents and some mechanistic aspects](#)

Kotohiro Nomura and Jingyu Liu

Dalton Trans., 2011, DOI: 10.1039/C1DT10086F

ARTICLES:

[Stoichiometric reactivity of dialkylamine boranes with alkaline earth silylamides](#)

Michael S. Hill, Marina Hodgson, David J. Liptrot and Mary F. Mahon

Dalton Trans., 2011, DOI: 10.1039/C1DT10171D

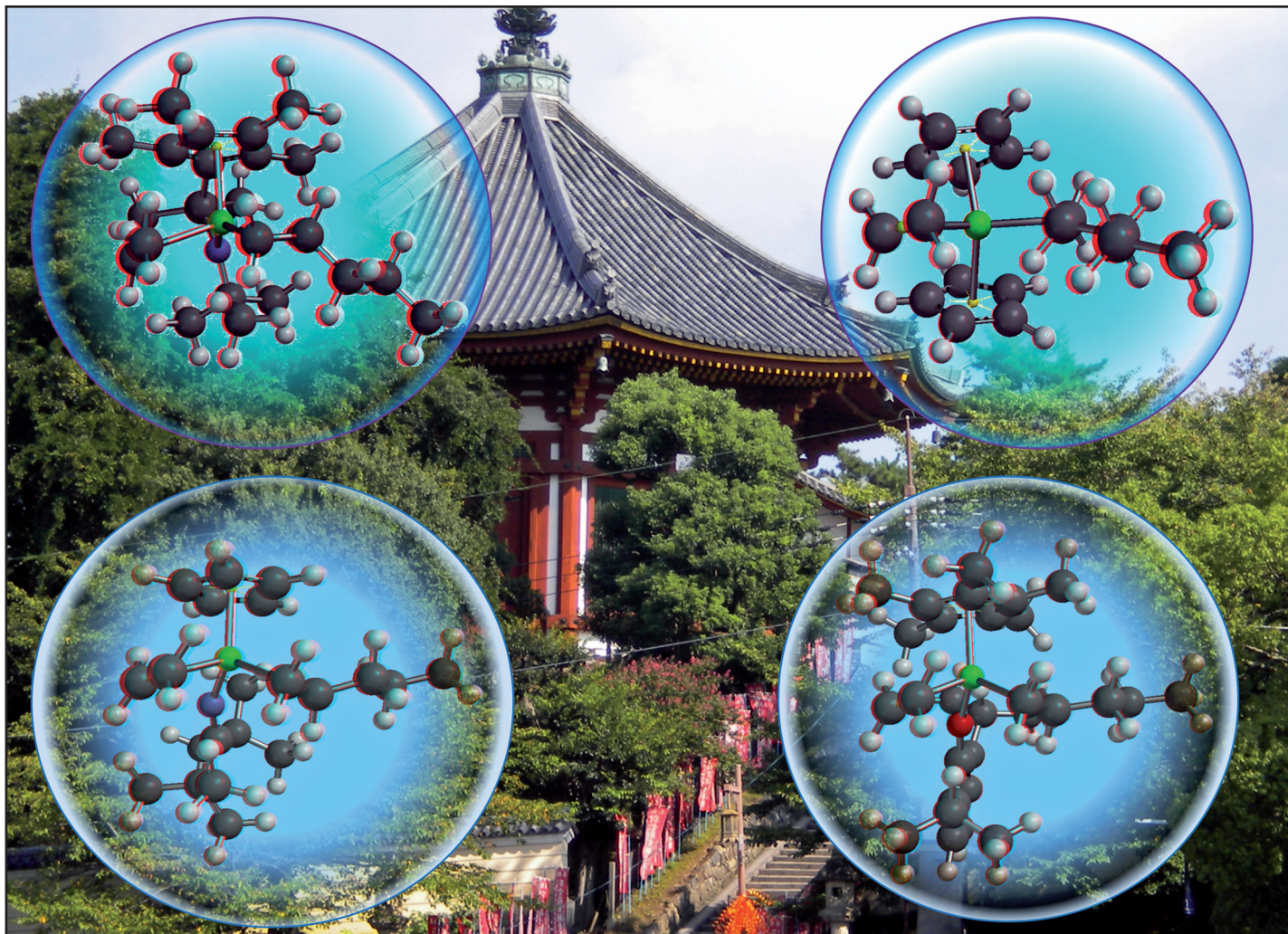
[Synthesis and reactivity of cationic niobium and tantalum methyl complexes supported by imido and \$\beta\$ -diketiminato ligands](#)

Neil C. Tomson, John Arnold and Robert G. Bergman

Dalton Trans., 2011, DOI: 10.1039/C1DT10202H

Visit the *Dalton Transactions* website for more cutting-edge inorganic and organometallic research

www.rsc.org/dalton



Selected examples concerning effects of both cyclopentadienyl fragment (Cp') and anionic donor ligand (Y) in non-bridged modified half-titanocenes of the type, Cp'TiX₂(Y) (X = halogen, alkyl), which display unique characteristics as new olefin polymerisation catalysts, have been reviewed; a precise fine tuning of the ligand substituents plays an important role for the successful (co)polymerisation.

Title: Half-titanocenes for precise olefin polymerisation: effects of ligand substituents and some mechanistic aspects (Perspective)

Showcasing research from the Organic Chemistry Laboratory (Prof. Dr. Kotohiro Nomura) at the Chemistry Department, Tokyo Metropolitan University (TMU), in collaboration with former/present group members (in TMU and Nara Institute of Science and Technology), partly funded by the Japan Society for the Promotion of Science (JSPS). The image describes four major catalytically-active species, and the background is the picture in the Nara Park, Japan (National Park).

As featured in:



See Nomura *et al.*, *Dalton Trans.*, 2011, **40**, 7666.

Cite this: *Dalton Trans.*, 2011, **40**, 7666

www.rsc.org/dalton

PERSPECTIVE

Half-titanocenes for precise olefin polymerisation: effects of ligand substituents and some mechanistic aspects

Kotohiro Nomura^{*a} and Jingyu Liu^b

Received 17th January 2011, Accepted 7th February 2011

DOI: 10.1039/c1dt10086f

Selected examples concerning effects of both cyclopentadienyl fragment (Cp') and anionic donor ligand (Y) in *nonbridged* modified half-titanocenes of the type, Cp'TiX₂(Y) (X = halogen, alkyl), as new type of olefin polymerisation catalysts have been reviewed. These complexes displayed unique characteristics not only for ethylene (co)polymerisation but also for syndiospecific styrene polymerisation, ethylene/styrene copolymerisation; precise *fine* tuning of the ligand substituents plays an important role for the successful (co)polymerisation; a different mechanistic consideration for the syndiospecific styrene polymerisation, which can explain the copolymerisation behaviour in this catalysis, has also been introduced.

Introduction

Polyolefins such as polyethylene [high density polyethylene (HDPE), linear low density polyethylene (LLDPE) *etc.*], polypropylene, produced by metal catalysed olefin coordination polymerisation, are important commercial synthetic polymers

^aDepartment of Chemistry, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo, 192-0397, Japan. E-mail: ktnomura@tmu.ac.jp

^bState Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academic Sciences, Changchun, 130022, China. E-mail: ljy@ciac.jl.cn



Kotohiro Nomura

Kotohiro Nomura finished his undergraduate study in Saitama University (1986), and accomplished his master degree from University of Tokyo (1988). He then joined Sumitomo Chemical Co., Ltd as a research scientist. He received his Ph.D. degree in 1993 from Osaka University, and joined a group of Prof. R. R. Schrock (Massachusetts Institute of Technology, Cambridge) as a postdoctoral fellow for two years. He then returned to Sumitomo, and moved to Nara Institute of Science and Technology as an Associate Professor in 1998. He has been a full professor in Department of Chemistry, Tokyo Metropolitan University since April, 2010. He has co-authored ca. 180 publications, and his recent research projects focus on design of molecular catalysts for precise olefin polymerisation, metathesis reactions, and chemospecific organic transformations.



Jingyu Liu

Jingyu Liu finished her undergraduate study in Changchun Institute of Technology (1994), and accomplished her master degree in the same university (1997). She then joined the group of Prof. Tian-Ru Fang [Changchun Institute of Applied Chemistry, Chinese Academic Sciences (CIAC)] as an assistant professor. She joined the group of Prof. Yue-Sheng Li (CIAC) for her Ph.D. course (2001), and started the research concerning olefin polymerisation. After receipt of her Ph.D. degree in 2005, she moved to a group of Prof. Nomura (Nara Institute of Science and Technology) as a JSPS postdoctoral fellow for two years. She then returned to the CIAC as the associate professor by merit-based selection at 2008. She has already published ca. 30 papers, and her recent research focused on design of transition metal catalysts for precisely controlled olefin polymerisation, and related organometallic chemistry.

in our daily life, and the market capacity still increases every year (especially in China, India, countries in the middle east).¹ Recently, considerable attention has been paid to produce new polymers with specified functions, exemplified by COCs (cyclic olefin copolymer, optical materials),² syndiotactic polystyrene (thermal, chemical resistance)³ and others. Since new polymers would be mostly prepared by incorporation of new comonomers (sterically encumbered, called *traditionally unreactive monomers* in transition metal catalysed coordination polymerisation) in the copolymerisation, it has thus been considered that design of the efficient transition metal complex catalysts that precisely control olefin coordination polymerisation should be the key for the success; recent progress in the new catalysts offers promising possibilities.^{2–15} Therefore, research focused on the design of efficient molecular catalysts for precise olefin polymerisation attracts considerable attention not only in the field of catalysis, organometallic chemistry, but also in the field of polymer chemistry.^{2–15}

As described above, the catalysts exhibiting remarkable activities with better comonomer incorporations are desired for the successful design of an efficient transition metal catalyst for ethylene (co)polymerisations. It has been reported that bridged (*ansa*) metallocene-type complexes show better comonomer incorporation than the nonbridged (unbridged) analogues in ethylene/ α -olefin copolymerisation,^{5,16} although both steric and electronic factors were affected toward the catalytic activity and molecular weight for resultant polymers in ethylene polymerisation by substituted zirconocenes.¹⁷ The fact has been explained as that the bridged metallocenes possess a rather large coordination space compared to the nonbridged analogues, allowing better accessibility for (rather) bulky α -olefins (Scheme 1).⁵ Linked half-titanocenes containing amide ligands, such as $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^i\text{Bu})]\text{TiCl}_2$ (**1**), so called “constrained geometry catalysts (CGC)”, have also been known to exhibit

efficient comonomer incorporation (Scheme 1),¹⁸ and the efficiency in α -olefin in ethylene/ α -olefin copolymerisation, that can be evaluated by using r_E values under the similar conditions, increases in the order: $\text{Cp}_2\text{ZrCl}_2 < \text{rac-Me}_2\text{Si}[\text{benz}(\text{e})\text{Ind}]_2\text{ZrCl}_2 < [\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^i\text{Bu})]\text{Ti-Cl}_2$.¹⁶ This CGC complex was designed according to the analogous scandium complex reported by Bercaw *et al.*¹⁹ and the reason for better comonomer incorporation has been explained as that the bridge constrains a more open Cp–Ti–N bond angle offering better comonomer incorporation by allowing improved accessibility for (rather) bulky α -olefins.^{5,6} Although recent results suggested that the coordination sphere is not the exclusive factor for the better comonomer incorporation,²⁰ many researchers focused on designing the catalysts with “constrained geometry type” for the above reason.^{6,18a}

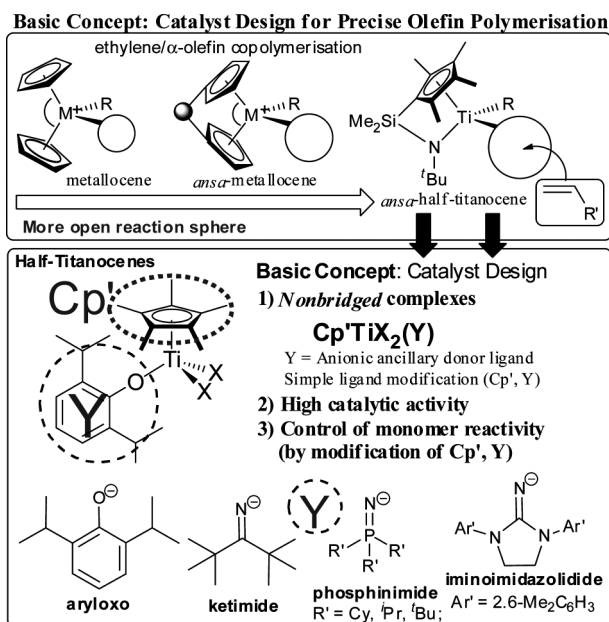
Nonbridged half-titanocenes of the type, $\text{Cp}'\text{TiX}_2(\text{Y})$ (Cp' = cyclopentadienyl group; Y = anionic donor ligand such as aryloxo,²¹ ketimide,^{22–25} phosphinimide,²⁶ iminoimidazolidide²⁷ *etc.*; X = halogen, alkyl), as shown in Scheme 1, have been considered as promising candidates for new efficient catalysts,^{2f,7,15,21–27} because, as described below, these complex catalysts display unique characteristics especially for the synthesis of new polymers^{7b,c,28–32} that cannot be prepared (or are very difficult to prepare) by ordinary catalysts such as Ziegler–Natta, metallocenes,⁵ ‘constrained geometry’ type catalysts (CGC),⁶ as exemplified in our previous feature article.^{7c} We first reported in May 1998^{21a} that half-titanocenes containing an aryloxo ligand of the type, $\text{Cp}'\text{TiCl}_2(\text{OAr})$ (Cp' = cyclopentadienyl group; OAr = aryloxo group, O-2,6-*i*-Pr₂C₆H₃ *etc.*), exhibited not only notable catalytic activities for olefin polymerisation, but also for efficient 1-butene incorporation in the ethylene/1-butene copolymerisation.^{21b,33–35} In the same year and later, there were several reports concerning synthesis of $\text{Cp}'\text{TiX}_2(\text{Y})$ and their use as catalysts for ethylene polymerisation.^{36–38} After these reports, as described below, many examples were reported describing syntheses of complexes of this type and their use as olefin polymerisation catalysts,^{7b,c} especially for ethylene polymerisation. In this article, we wish to review the selected reported complex catalysts and present some unique characteristics that can be seen in this catalysis.

1. Nonbridged half-titanocenes as olefin polymerisation catalysts

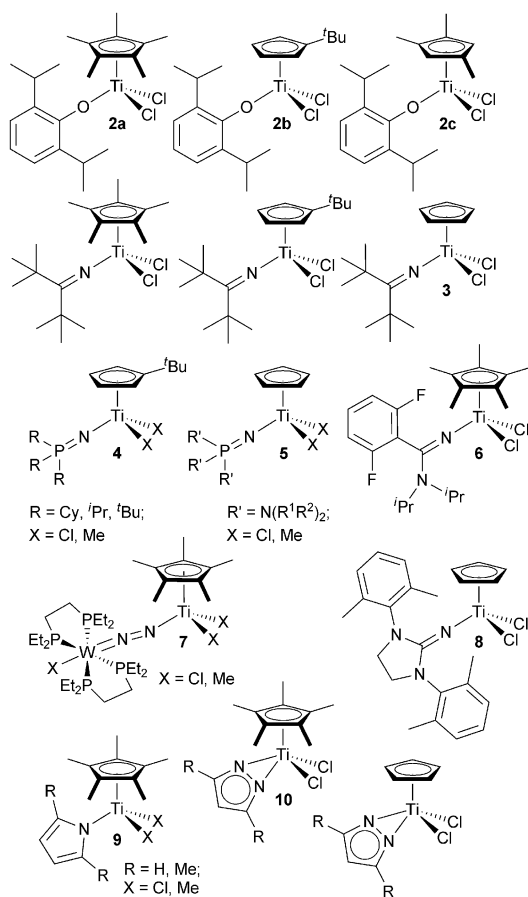
Selected examples of half-titanocenes containing anionic donor ligands, $\text{Cp}'\text{TiX}_2(\text{Y})$, are shown in Scheme 2.^{7,21–27,36–40} Many examples were reported for synthesis of complexes of this type and their use as olefin polymerisation catalysts, especially for ethylene polymerization: some examples were known to exhibit remarkable activities, as described below.

1.1 Olefin polymerisation by half-titanocenes containing aryloxo ligands

It has been known that the ligand modification is very important in order for metal catalysed olefin polymerisation to proceed with remarkable activities. For example, as shown in Tables 1,2, both substituents on cyclopentadienyl and aryloxo ligands affected the activity for ethylene polymerisation.^{21a,b} $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)$ (**2a**) exhibited notable activities, and the activity by



Scheme 1 Basic proposed concept for the catalyst design and selected examples for half-titanocenes as effective catalyst precursors for olefin polymerisation.^{5–7}



Scheme 2 Selected half-titanocenes exemplified in this article as effective catalyst precursors.

$\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ increased in the order: $\text{Cp}^* = \text{Cp}^* \gg 1,3\text{-}i\text{Bu}_2\text{C}_5\text{H}_3 > 1,3\text{-Me}_2\text{C}_5\text{H}_3, \text{}^i\text{BuC}_5\text{H}_4 \gg \text{Cp}$ (Table 1).

This seems to be a similar observation for syndiospecific styrene polymerisation using a series of $\text{Cp}^*\text{Ti}(\text{OME})_3$ complexes,^{15a,41} and

Table 1 Effect of cyclopentadienyl fragment (Cp') toward the activity in olefin polymerisation by $\text{Cp}'\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ -MAO catalyst systems^a

Cp' (μmol)	Olefin	Activity ^b	TON ^c	$10^{-4}M_w^d$	M_w/M_n^d
Cp (18.3)	Ethylene	77	2750		
Cp (5.0)	1-Hexene	62	370	0.68	
$^i\text{BuC}_5\text{H}_4$ (15.1)	Ethylene	258	9200	5.99	2.1
$^i\text{BuC}_5\text{H}_4$ (5.0)	1-Hexene	90	532	8.04	1.6
$^i\text{BuC}_5\text{H}_4$ (5.0)	1-Octene	125	558	8.25	1.9
1,3-Me ₂ C ₅ H ₂ (24.2)	Ethylene	215	7660	1.75	2.5
1,3-Me ₂ C ₅ H ₂ (5.0)	1-Hexene	184	1090	8.73	1.9
1,3- $^i\text{Bu}_2\text{C}_5\text{H}_2$ (5.0)	Ethylene	653	23300	64.9	6.8
1,3- $^i\text{Bu}_2\text{C}_5\text{H}_2$ (5.0)	1-Hexene	26	152	2.16	1.6
1,3- $^i\text{Bu}_2\text{C}_5\text{H}_2$ (5.0)	1-Octene	38	168	1.75	1.5
Cp^* (6.5)	Ethylene	2220	79100	45.9	5.0
Cp^* (1.0)	1-Hexene	728	4330	69.4	1.6
Cp^* (1.0)	1-Octene	970	4320	49.5	1.8
Cp^* (1.0)	1-Decene	1036	3690	41.7	1.7

^a Cited from refs. 21a,b,e. Conditions: ethylene 4 atm, 60 °C, 1 h, toluene 300 mL, $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Al}^i\text{Bu}_3/\text{Ti} = 1/500/1$ (molar ratio);^{21a,b} α -olefin 5 mL, catalyst 2 $\mu\text{mol mL}^{-1}$ toluene, MAO white solid, 25 °C, 30 min.^{21e}
^b Activity in kg-polymer/mol-Ti-h. ^c TON (turnover numbers) = molar amount of olefin reacted/mol-Ti. ^d By GPC vs. polystyrene standards.

Table 2 Effect of aryloxy substituents toward the activity in ethylene polymerisation by $\text{Cp}^*\text{TiCl}_2(\text{O}-2\text{-R}^1\text{-4-R}^2\text{-6-R}^3\text{-C}_6\text{H}_2)$ -MAO catalyst systems^a

$\text{R}^1, \text{R}^2, \text{R}^3$ (μmol)	Activity ^b	TON ^c	$10^{-4}M_w^d$	M_w/M_n^d
$^i\text{Pr}, \text{H}, ^i\text{Pr}$ (4.2)	1240	43100	64.9	4.7
H, Me, H (13.0)	25	890		
Me, H, Me (4.0)	1000	35700	123	4.5
$^i\text{Bu}, \text{Me}, \text{Me}$ (13.0)	446	15900		
Me, Me, Me (8.4)	369	13200		

^a Cited from ref. 21b. Conditions: ethylene 4 atm, 60 °C, 1 h, toluene 300 mL, MAO (Al/Ti = 1000, molar ratio). ^b Activity in kg-polymer/mol-Ti-h. ^c TON (turnover numbers) = molar amount of reacted olefin/mol-Ti. ^d By GPC vs. polystyrene standards.

the similar explanation that stabilization of the active site by more electron-donating substituents is important for the high activity can be thus assumed. The $^i\text{Bu}_2\text{Cp}$ analogue showed lower catalytic activity in 1-hexene and 1-octene polymerisation due to the steric bulk on Cp' .^{21c,e} It should also be noteworthy that the observed activities were of a similar level between 1-hexene and 1-octene polymerisations.^{21c,e}

Steric bulk of the phenoxy ligand containing substituents in the 2,6-position should be important for exhibiting the high activity (Table 2).^{21a,b} We assumed that the steric bulk plays a role to stabilise the catalytically-active species under the polymerisation conditions in the presence of co-catalyst (in addition to protect the probable accompanied reaction with Al alkyls, dissociation of the aryloxyde).

More recently, we explored effect of the centered metal toward the catalytic activity as well as comonomer incorporation in ethylene (co)polymerisation using a series of $\text{Cp}^*\text{MCl}_2(\text{O}-2,6\text{-R}_2\text{C}_6\text{H}_3)$ (M = Ti, Zr, Hf; R = Ph, ^iBu , ^iPr) in the presence of MAO co-catalyst.⁴² The activity in ethylene polymerisation was affected by the metal center employed [Ti > Zr > Hf];^{42,43} the Ti-2,6-diphenylphenoxy analogue showed higher activities than the Ti-2,6-di-*tert*-butylphenoxy analogue. Although the copolymerisations of ethylene with 1-octene using the titanium complexes afforded the copolymers with uniform molecular weight distributions (except the *tert*-butyl analogue); the isopropyl analogue (**2a**) seems to be the most suited in terms of both the activity and the 1-octene incorporation. The attempted copolymerisation of ethylene with 2-methyl-1-pentene using both the phenyl and the *tert*-butyl analogues afforded linear polyethylene.⁴²

In order to explore the reason why both the Cp^* and 2,6-diisopropylphenoxy ligand in **2a** are prerequisite for the remarkable activity in the ethylene polymerisation, we prepared various Cp and aryloxy analogues and determined the structures by X-ray crystallography.^{21a,b} As shown in Table 3, the bond angle (173.0°) of Ti–O–C (phenoxy) for $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (**2a**), which was the most effective catalyst precursor, is significantly different from those for the other 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 Cp^* and the diisopropyl group sterically force the more open Ti–O–C bond angle, which leads to more O→Ti π donation into Ti; this along with the more electron donating Cp^* (as compared with Cp, $^i\text{BuC}_5\text{H}_4, 1,3\text{-Me}_2\text{C}_5\text{H}_3$) stabilises the active species, leading to the higher activity.^{21a,b}

Table 3 Selected bond distances (Å) and angles (°) for Cp^{*}TiCl₂(O-2,6-*i*-Pr₂C₆H₃)^{21a,b}

Cp [*] TiCl ₂ (O-2,6- <i>i</i> -Pr ₂ C ₆ H ₃)	Cp	Cp [*]	1,3- <i>i</i> -Bu ₂ C ₅ H ₃
Ti(1)–Cl(1)	2.262	2.305	2.2553
Ti(1)–C(1) (Cp [*])	2.282	2.367	2.379
Ti(1)–C(3) (Cp [*])	2.325	2.368	2.41
Ti(1)–Cp [*]	1.99	2.03	2.04
Ti(1)–O(1)	1.76	1.772	1.773
O(1)–C(6)	1.368 ^a	1.367	1.365
Cl(1)–Ti(1)–Cl(2)	104.23	103.45	103.46
Cl(1)–Ti(1)–O(1)	102.53	99.1	103.62
Cl(2)–Ti(1)–O(1)	102.53	104.1	98.57
Ti(1)–O(1)–C(6)	163.0 ^a	173	163.1
Cp–Ti(1)–O(1)	117.6	120.5	119.3
Cp–Ti(1)–Cl(1)	114.1	111.1	114.3
Cp–Ti(1)–Cl(2)	114.1	116.1	115.2

^a O(1)–C(4) or Ti(1)–O(1)–C(4).

Table 4 summarises selected results for bond distances and angles in the various Cp^{*}-aryloxy analogues.^{21a,b,34,44–46} 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*-Pr₂C₆H₃, 2,6-*i*-Pr₂-4-*i*-BuC₆H₂, respectively)^{21a,b,44} were larger than those in the other Cp^{*} derivatives (155.5–162.3°) except Cp^{*}TiCl₂(O-2,6-Ph₂-3,5-*i*-Bu₂C₆H₃) (176.9°).³⁴ Although we assumed above that both Cp^{*} and diisopropyl group ‘sterically’ force the more open Ti–O–C bond angle, the bond angle for the di-*tert*-butyl analogue was small (155.5°).⁴⁴ A similar large bond angle was observed in Cp^{*}TiCl₂(O-2,6-Ph₂-3,5-*i*-Bu₂C₆H₃) whereas the value in Cp^{*}TiCl₂(O-2,6-Ph₂C₆H₃) was rather small (160.6°).

The results might suggest that the unique bond angle would be dependent upon the ligand set employed, and it is thus suggested that the unique bond angles in Ti–O–C (phenyl) were affected by substituents in both cyclopentadienyl and aryloxy ligands. The results suggest that the unique bond angles in Ti–O–C (phenyl) affect the high activity by more O→Ti π donation into the titanium, leading to stabilise the catalytically-active species for exhibiting the higher activity.

Since the unique bond angle in Ti–O–C(phenyl) seems to be originated from the ligand set (Cp^{*} and 2,6-diisopropylphenoxy), we prepared, determined the structures Cp^{*}Ti(X¹)(X²)(O-2,6-*i*-Pr₂-4-R^{*}C₆H₂) (X¹, X² = Cl, Cl, Me, Me, Me, CF₃SO₃, R^{*} = H or *i*-Bu) by X-ray crystallography.⁴⁷

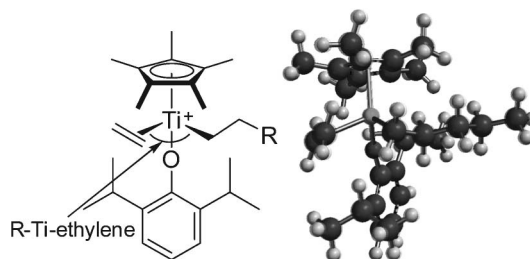
Table 4 Selected bond distances (Å) and angles (°) for Cp^{*}TiCl₂(O-2,6-R₂-4-R^{*}C₆H₂)^{21a,34,44–46}

R, R [*]	Me, H ^a	Me, Me ^b	<i>i</i> -Pr, H ^c	<i>i</i> -Pr, <i>i</i> -Bu ^b	<i>i</i> -Bu, H ^b	Ph, H ^d	Ph, 3,5- <i>i</i> -Bu ₂ ^e
Ti(1)–Cl(1)	2.273	2.262	2.305	2.268	2.2674	2.2693	2.258
Ti(1)–C(1) (Cp)	2.329	2.344	2.367	2.345	2.359	2.355	2.340
Ti(1)–C(3) (Cp)	2.398	2.374	2.368	2.399	2.370	2.377	2.420
Ti(1)–O(1)	1.785	1.781	1.772	1.779	1.804	1.811	1.804
Cl(1)–Ti–Cl(2)	103.3	103.2	103.45	103.68	98.10	98.70	100.44
Cl(1)–Ti–O(1)	101.7	102.0	99.1	102.73	103.22	104.33	103.68
Cl(2)–Ti–O(1)	101.7	101.6	104.1	101.83	103.22	105.20	104.34
Ti–O–C(6) (Ph)	162.3	162.1	173.0	174.6	155.5	160.6	176.90

^a Cited from ref. 45. ^b Cited from ref. 44. ^c Cited from ref. 21a. ^d Cited from ref. 46. ^e Cited from ref. 34.

Although no notable differences in the bond distances were observed among these complexes, the bond angles in X¹–Ti–X² were influenced by the anionic ligands (X¹, X²), probably due to the increased steric bulk of Me, CF₃SO₃ ligands compared to Cl. It is noteworthy that the bond angles in Ti–O–C(phenyl) were somewhat large in all cases (166.2–174.6°), clearly suggesting that both Cp^{*} and the 2,6-diisopropyl-substituted aryloxy ligand form the unique bond angle, leading to more O→Ti π donation into the titanium.

Geometry optimisations of the proposed catalytically active species, [Cp^{*}Ti(pentyl)(OAr)(ethylene)]⁺ (Fig. 1), with a series of cyclopentadienyl and aryloxy ligands were thus simply calculated to explore the ligand effects in this catalysis on the basis of [Cp^{*}Ti(pentyl)(O-2,6-*i*-Pr₂C₆H₃)(ethylene)]⁺, which should be most suited from the experimental facts, and the results are summarised in Table 5. As reported previously,⁴¹ introduction of methyl group (or *tert*-butyl group) onto Cp^{*} leads to stabilisation of the catalytically-active species (C₅Me₅ > Me₃C₅H₂ > Me₂C₅H₂ > C₅H₅). Aryloxy substituent in the *ortho* position not only affects the stabilisation, but also affects the R–Ti–ethylene bond angle that should be important for the subsequent insertion. It was revealed that the cationic species containing Cp^{*} and diisopropylphenoxy ligands showed both better stabilisation and possessed geometry for the subsequent insertion (narrow bond angle). Although the results are on the basis of simple PM3 semiempirical level, we believe this would be the origin why **2a** showed the high activity affording the polymer with unimodal distributions in this catalysis.

**Fig. 1** Assumed catalytically-active species, the optimised structure.⁴⁸

The observed catalytic activity was extremely low if B(C₆F₅)₃ was used as the co-catalyst for 1-hexene polymerisation in the presence of Cp^{*}TiMe₂(O-2,6-*i*-Pr₂C₆H₃)-AlⁱBu₃ catalyst system, although significant catalytic activity was observed if

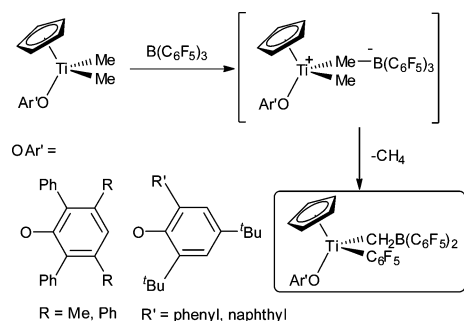
Table 5 Effect of ligand by energy evaluations of the catalytically-active species by semi-empirical PM3 geometry optimisation^{a, 48}

Cp, OAr'	ΔE^a /kcal mol ⁻¹	R-Ti-ethylene/ ^o
Cp*, O-2,6-'Pr ₂ C ₆ H ₃	0	85.3
Me ₂ C ₃ H ₂ , O-2,6-'Pr ₂ C ₆ H ₃	10.1	87.2
Me ₂ C ₃ H ₃ , O-2,6-'Pr ₂ C ₆ H ₃	15.7	86.9
MeC ₃ H ₄ , O-2,6-'Pr ₂ C ₆ H ₃	18.4	87.0
Cp, O-2,6-'Pr ₂ C ₆ H ₃	25.1	86.7
'BuC ₃ H ₄ , O-2,6-'Pr ₂ C ₆ H ₃	7.7	88.8
Cp*, 4-MeC ₆ H ₄	27.7	83.6
Cp*, 2,6-Me ₂ C ₆ H ₃	15.3	88.0
Cp*, 2,6-'Pr ₂ C ₆ H ₃	0	85.3
Cp*, 2-'Bu-4,6-Me ₂ C ₆ H ₃	-6	97.4
Cp*, 2,6-'Bu ₂ C ₆ H ₃	-1.8	76.7

^a Compared with [Cp*Ti(O-2,6-'Pr₂C₆H₃)(pentyl)(ethylene)]⁺, equilibrium geometry at ground state with semi-empirical PM3, geometry optimisation, RHF/PM3D Spartan '08 for Windows (Wavefunction Inc.).

[Ph₃C][B(C₆F₅)₄] was used in place of B(C₆F₅)₃.⁴⁹ The polymerisation took place in a quasi-living manner with remarkably high catalyst efficiency even at -30 °C, when both [Ph₃C][B(C₆F₅)₄] and AlⁱBu₃ were used as co-catalysts under the optimised conditions. The resultant poly(1-hexene) possessed high molecular weight with narrow molecular weight distribution ($M_n = 1.87 \times 10^6$, $M_w/M_n = 1.27$).⁴⁹ The reaction with B(C₆F₅)₃ in toluene-*d*₈ afforded decomposed compound, Cp*Ti(C₆F₅)[CH₂B(C₆F₅)₂](O-2,6-'Pr₂C₆H₃), (and/or intermediates) even at -70 °C, whereas no decomposition was observed if the reaction of **1b** was employed with [Ph₃C][B(C₆F₅)₄].⁴⁷ 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 co-catalysts in the 1-hexene polymerisation.

Rothwell *et al.* also prepared a CpTiMe₂(OAr) complex containing an *ortho*-naphthylphenoxide ligand,³⁴ and addition of B(C₆F₅)₃ in benzene gave thermally unstable cationic complex, CpTiMe[μ-Me)B(C₆F₅)₃](OAr) (**2**), which then gradually decomposed at ambient temperature to afford the neutral species, CpTi(C₆F₅)[CH₂B(C₆F₅)₂](OAr), followed by methane elimination (Scheme 3).³⁴

**Scheme 3** Deactivation pathway by reacting with B(C₆F₅)₃.³⁴

1.2. Selected examples in olefin polymerisation by half-titanocenes containing other anionic ancillary donor ligands

Stephan *et al.* focused on using a sterically bulky phosphinimide ligand as the steric equivalent to cyclopentadienyl group,²⁶

Table 6 Ethylene polymerisation by Cp'TiX₂(N=PR₃) [**4**, Cp' = Cp, 'BuC₃H₄ ('BuCp); X = Cl, Me; R = Cy, 'Pr, 'Bu] co-catalyst systems^a

Complex	Co-cat.	Activity ^b	10 ⁻⁴ M _w ^c	M _w /M _n ^c
CpTiCl ₂ (N=PCy ₃)	MAO	42	0.36 ^d	1.8
			33.6	2.2
CpTiCl ₂ (N=P'Pr ₃)	MAO	49	1.87 ^d	2.8
			57.9	2.4
CpTiCl ₂ (N=P'Bu ₃)	MAO	500	8.99	2.4
CpTiMe ₂ (N=PCy ₃)	Ph ₃ CB(C ₆ F ₅) ₄	231	13.5	2.8
CpTiMe ₂ (N=P'Pr ₃)	Ph ₃ CB(C ₆ F ₅) ₄	225	16.4	3.4
CpTiMe ₂ (N=P'Bu ₃)	Ph ₃ CB(C ₆ F ₅) ₄	401	16.6	3.4
'BuCpTiCl ₂ (N=PCy ₃)	MAO	46	0.74 ^d	2.1
			89.4	3.4
'BuCpTiCl ₂ (N=P'Pr ₃)	MAO	16	0.76 ^d	1.9
			91	2.5
'BuCpTiCl ₂ (N=P'Bu ₃)	MAO	881	6.54	2.4
'BuCpTiMe ₂ (N=PCy ₃)	Ph ₃ CB(C ₆ F ₅) ₄	1807	31	7.5
'BuCpTiMe ₂ (N=P'Pr ₃)	Ph ₃ CB(C ₆ F ₅) ₄	1193	25.9	9.9
'BuCpTiMe ₂ (N=P'Bu ₃)	Ph ₃ CB(C ₆ F ₅) ₄	1296	32.1	12.3
[Me ₂ Si(C ₅ Me ₄)(N'Bu)]TiCl ₂	MAO	630		

^a Cited from ref. 26a. *Conditions*: catalyst 0.01–0.03 mmol, toluene, ethylene 1 atm, 25 °C, 0.5–3 min, MAO (Al/Ti = 500, molar ratio) or Ph₃CB(C₆F₅)₄ (B/Ti = 2). ^b Activity in kg-polymer/mol-Ti·h. ^c GPC data vs. polyethylene standards. ^d Bimodal molecular weight distributions.

because the bulky ligand would provide an environment sterically/electronically similar to the cyclopentadienyl fragment.⁵⁰ A series of half-titanocenes containing phosphinimide ligand of type, Cp'Ti(N=PR₃)X₂ (**4**, Scheme 2), were employed to explore the effect of the substituents on both Cp' and N=PR₃ groups for the activity in ethylene polymerisation (Table 6).²⁶ These complexes exhibited remarkable catalytic activities in the presence of MAO, and the activity improved with the combination of [Ph₃C][B(C₆F₅)₄]. Substituents on both Cp' and N=PR₃ ligands play an essential role for exhibiting the high activity, and use of N=PCy₃ ligand was effective. The 'BuC₃H₄ analogues were more suited than the Cp analogues, suggesting that electron-donating substituents on Cp' increase the activity. Analogous zirconium complexes were also prepared, but these complexes showed low activities for ethylene polymerisation in the presence of MAO,^{51a} the activities by the Zr analogues improved upon the presence of [Ph₃C][B(C₆F₅)₄] co-catalyst.^{51b}

DFT calculations of the mechanism of polymerisation by a series of catalyst models derived from CpTiMe₂(N=PR₃) (R = Me, NH₂, H, Cl, F) demonstrated the critical role of ion pairing in determining the overall barrier to polymerisation, and suggested that the ligands containing electron-donating substituents would reduce the barrier.⁵² The tris-amido-phosphinimide analogues, Cp'TiX₂[N=P(NR₂)₃] (**5**, X = Cl, Me), showed notable catalytic activities in the presence of borate-based activators (Table 7),⁵² and the activity increased upon increasing the steric bulk. Optimisation 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.

In contrast, as shown in Table 8, no significant differences in the activities were observed in ethylene polymerisation using Cp'TiCl₂(N=C'Bu₂) [Cp' = Cp, Bu'C₃H₄, Cp*].²⁴ However, the activities in 1-hexene polymerisations were highly dependent upon the Cp' employed (Table 9).²⁴ The polymerisation by the Cp

Table 7 Ethylene polymerisation by Cp'TiX₂[NP(NR¹R²)₃] (**5**)–co-catalyst systems^a

Precatalyst (μmol L ⁻¹)	Co-cat.	t/min	Activity ^b	10 ⁻⁴ M _n ^c	M _w /M _n ^c
Cp*TiCl ₂ [N=P(NMe ₂) ₃] (100)	MAO	30	21	82.6	1.72
Cp*TiCl ₂ [N=P(NEt ₂) ₃] (100)	MAO	30	39	9.01	1.65
Cp*TiCl ₂ [N=P{N(Me)Pr ₂ } ₃] (50)	MAO	30	56	12.78	2.76
Cp*TiCl ₂ [N=P{N(Et)Ph} ₃] (50)	MAO	30	200	12.61	4.02
CpTiMe ₂ [N=P(NMe ₂) ₃] (4)	Al/B ^d	10	2200	31.5	2.05
CpTiMe ₂ [N=P(NEt ₂) ₃] (4)	Al/B ^d	10	3500	39.4	1.91
CpTiMe ₂ [N=P(NPr ₂) ₃] (4)	Al/B ^d	10	5500		
CpTiMe ₂ [N=P(NBu ₂) ₃] (4)	Al/B ^d	10	3600		
CpTiMe ₂ [N=P{N(Me)Pr ₂ } ₃] (4)	Al/B ^d	10	3600	38.86	1.85
CpTiMe ₂ [N=P{N(Et)Ph} ₃] (4)	Al/B ^d	10	4200	43.25	1.92
Cp*TiMe ₂ [N=P(NMe ₂) ₃] (4)	Al/B ^d	10	4200	14.08	4.92
Cp*TiMe ₂ [N=P(NEt ₂) ₃] (4)	Al/B ^d	10	4700		
Cp*TiMe ₂ [N=P(NPr ₂) ₃] (4)	Al/B ^d	10	10000		
Cp*TiMe ₂ [N=P(NBu ₂) ₃] (4)	Al/B ^d	10	6100		
Cp*TiMe ₂ [N=P{N(Me)Pr ₂ } ₃] (4)	Al/B ^d	10	4900	28.81	2.14
Cp*TiMe ₂ [N=P{N(Et)Ph} ₃] (4)	Al/B ^d	10	4200	32.46	2.03
Cp*TiMe ₂ [N=P'Pr ₃] (4)	Al/B ^d	10	5200	49.34	2.05
CpTiMe ₂ [N=P'Bu ₃] (4)	Al/B ^d	10	5600	43.78	1.8
Cp ₂ ZrMe ₂ (4)	Al/B ^d	10	16000	17.5	1.89

^a Cited from ref. 52. *Conditions*: ethylene 2 atm at 30 °C, toluene 600 mL, stir rate = 1000 rpm, 500 equiv. of MAO or Al/B. ^b Activity in kg-PE/mol-Ti-h-atm. ^c GPC data in *o*-dichlorobenzene. ^d Al/B = Al'Bu₃/B(C₆F₅)₃, 2 equiv. of B(C₆F₅)₃; 20 equiv. of Al'Bu₃.

Table 8 Ligand effect in ethylene polymerisation by Cp'TiCl₂(N=C'Bu₂) (Cp' = Cp, 'BuC₃H₄, Cp*, indenyl)–MAO catalyst systems^a

Cp'	Ethylene/atm	Activity ^b	10 ⁻⁵ M _w ^c	M _w /M _n ^c
Cp	4	13400	9.66	1.9
Cp	6	22100	9.84	1.9
'BuC ₃ H ₄	4	14300	9.9	2.1
Cp*	4	16600	10.4	2.2
indenyl	4	7700	5.61	2.1

^a Cited from ref. 24. *Conditions*: complex 0.2 μmol, toluene 40 mL, MAO white solid 3.0 mmol (Al), 40 °C, 10 min. ^b Activity in kg-PE/mol-Ti-h. ^c GPC data in *o*-dichlorobenzene vs. polystyrene standards.

Table 9 1-Hexene polymerisation by Cp'TiCl₂(N=C'Bu₂) (Cp' = Cp, 'BuC₃H₄, Cp*, indenyl)–MAO catalyst systems^a

Cp' (μmol)	Activity ^b	10 ⁻³ TON	10 ⁻⁴ M _n ^c	M _w /M _n ^c
Cp (0.25)	16800	66.8	61.7	1.6
'BuC ₃ H ₄ (2.5)	1310	5.21	28.5	1.7
Cp* (2.5)	569	2.26	13.0	1.6
Indenyl (0.25)	11900	47.2	28.1	1.7

^a Cited from ref. 24. *Conditions*: complex in toluene 0.5 mL, 1-hexene 10 mL, 25 °C, 20 min, MAO white solid 2.0 mmol. ^b Activity in kg-polymer/mol-Ti-h. ^c GPC data in THF vs. polystyrene standards.

analogue, CpTiCl₂(N=C'Bu₂), took place efficiently, and a first-order relationship between the monomer concentration and the reaction rate was observed in the time-course plots vs. ln[M]/[M]₀, strongly suggesting that the apparent decrease is due to the decrease in the 1-hexene concentration not due to the deactivation of catalytically-active species.

The activities by Cp'TiCl₂[N=C(R¹)R²] were strongly affected by the substituents in the ketimide ligands (Table 10 and 11).^{23,30d} CpTiCl₂(N=C'Bu₂) (**3**) exhibited higher catalytic activity (Table 10) than CpTiCl₂[N=C(Me)Ph]. The activities in ethylene polymerisation with a series of CpTiCl₂[N=C(R¹)R²]–MAO catalyst

Table 10 Ethylene polymerisation with Cp'TiX₂(N=CR₂) [Cp' = Cp, C₅Me₅, indenyl, C₄Me₄P; R = 'Bu, NMe₂ etc.]–MAO catalyst systems. Slurry polymerisation results^a

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

^a Cited from ref. 23. *Conditions*: catalyst 15.2 μmol, cyclohexane 300 mL, MAO (PMAO-IP), Al/M = 500, ethylene 10 psig (0.68 atm), 35 °C, 30 min.

systems under the optimised Al/Ti ratios increased in the order: R¹, R² = 'Bu, 'Bu (5880 kg-PE/mol-Ti-h) ≫ 'Bu, Ph (90.0) > Ph, Ph (56.4) (Table 11).^{30d} The same trend in the activity was observed by the Cp* analogues. The results would suggest that an electronic nature of the ketimide ligand affects the activity, but the resultant PEs prepared by the diphenyl or *tert*-butylphenyl analogues possessed multi-modal molecular weight distributions, consisting of a mixture of high and low molecular weight polymers. The same trend was also observed in the ethylene/norbornene copolymerisation using CpTiCl₂[N=C(R¹)R²]–MAO catalyst systems (except **3**).^{30d} The complexes containing two 'Bu groups in the ketimide ligand, Cp'TiCl₂(N=C'Bu₂), were thus effective for these (co)polymerisations to give polymers with unimodal molecular weight distributions, in other words, to proceed with uniform catalytically-active species.

According to a recent patent by DSM,³⁷ Cp*TiX₂[N=C(2,6-R¹₂C₆H₃)(NR²)₂] [**6**, Scheme 2, R¹ = F, Cl; R² = 'Pr, Cy etc.; X = Cl, Me] exhibited remarkable catalytic activities for copolymerisation of ethylene with propylene (for synthesis of EPDM, ethylene-propylene–diene copolymer), and the activity was also

Table 11 Ethylene polymerisation by Cp^{*}TiCl₂[N=C(R¹)R²] [Cp^{*} = Cp, Cp^{*}; R¹, R² = ⁱBu, ⁱBu, ⁱBu, Ph or Ph, Ph] or Cp^{*}TiCl₂(O-2,6-ⁱPr₂C₆H₃) (2)–MAO catalyst systems^a

Cp [*]	R ¹ , R ²	Amount/μmol	Activity ^b	10 ⁻⁴ M _n ^c	M _w /M _n ^c
Cp	ⁱ Bu, ⁱ Bu (3)	0.1	5880	45.2	2.30
Cp	ⁱ Bu, Ph	5.0	90.0	Multi-modal ^d	
Cp	Ph, Ph	5.0	56.4	Multi-modal ^d	
Cp [*]	ⁱ Bu, ⁱ Bu	0.05	19680	42.2	2.45
Cp [*]	Ph, Ph	5.0	126	Multi-modal ^d	
Cp [*]	O-2,6- ⁱ Pr ₂ C ₆ H ₃ (2)	0.2	8400	65.2	1.90

^a Cited from ref. 30d. *Conditions*: toluene 50 mL, MAO white solid 3.0 mmol, ethylene 4 atm, 25 °C, 10 min. ^b Activity in kg-PE/mol-Ti·h. ^c GPC data in *o*-dichlorobenzene vs. polystyrene standards. ^d Multi-modal molecular weight distributions.

Table 12 Ethylene homopolymerisation and ethylene/1-hexene copolymerisation catalysed by heterobimetallic dinitrogen complex (7)^a

Catalyst (μmol)	Co-cat. ^b	Activity ^c	10 ⁻⁴ M _w ^c	M _w /M _n ^c	1-Hexene ^d
7 (0.1)	Al/B	61000	45	4.8	
7 (0.1)	MMAO	56000	121	15.2	
7 (0.025) ^e	Al/B ^e	416000	58	2.1	2.15
CGC (0.1)	Al/B	21000	31	4.1	
CGC (0.1)	MMAO	800	50	5.4	
CGC (0.025) ^e	Al/B ^e	120000	38	4.2	8.49

^a Cited from ref. 38. *Conditions*: toluene 200 mL, ethylene 6 atm, 60 °C, 1 h, catalyst 0.1 μmol. ^b MMAO 0.5 mmol or Al/B = AlⁱBu₃/[Ph₃C][B(C₆F₅)₄] = 0.25/0.001 mmol. ^c Activity in kg-polymer/mol-Ti·h. ^d 1-Hexene content in mol%, estimated by ¹³C NMR spectra. ^e AlⁱBu₃ 0.25 mmol, [Ph₃C][B(C₆F₅)₄] 1.0 μmol.

highly affected by the substituents (R¹, R²); Cp^{*}TiX₂[N(2,6-F₂C₆H₃)(NⁱPr₂)] exhibited notable activity,^{37a} they also described that these complexes were also effective for synthesis of ultra-high molecular weight polyethylene.

Ethylene polymerisation and copolymerisation of ethylene with 1-hexene catalysed by heterobimetallic dinitrogen complex (7, Scheme 2) were reported.³⁸ The complex exhibited high catalytic activities, but the 1-hexene incorporation was not sufficient probably due to bulky substituent in the anionic donor ligand (Table 12).

Kretschmer and Hessen reported that half-titanocenes containing 1,3-bis(xylyl)iminoimidazolidide ligand, CpTi(CH₂-Ph)₂[N=C[{N(2,6-Me₂C₆H₃)CH₂}₂]] (8, Scheme 2) exhibited notable catalytic activities for ethylene polymerisation in the presence of B(C₆F₅)₃ co-catalyst.²⁷ As shown in Table 13, they emphasised that the catalyst showed higher catalytic activities

than the CpTi(CH₂Ph)₂(NPⁱBu₃) under the same conditions (in the presence of partially hydrolyzed AlⁱBu₃, TIBAO). No polymerisation results in the presence of MAO were referred to.²⁷ They also introduced the results for copolymerisation of ethylene with α-olefin, styrene, norbornene, but the comonomer incorporations were not as high as those by the aryloxo^{21,32} or ketimide analogues.³⁰

Taking into account the facts described above, the role of anionic donor ligand should be the key for design of more effective catalyst precursors in this catalysis.

Half-titanocenes containing various pyrrolide ligands, Cp^{*}TiCl₂(Y) (9, Scheme 2), were prepared and their use as catalyst precursors for ethylene polymerisation were explored.³⁹ The Cp^{*} analogues exhibited higher catalytic activity than the Cp analogues in the presence of MAO (Table 14); Cp^{*}TiCl₂(C₄H₄N) exhibited the highest catalytic activity. Both electronic and steric factors affected the activity. However, the resultant polymers prepared by the dichloride analogue–MAO catalysts systems possessed trace amounts of low or high molecular weight shoulders, probably due to dissociation of the pyrrolide ligand by Al in the catalytic reaction in the presence of MAO (Fig. 2). The resultant polymers possessed unimodal molecular weight distributions when the polymerisations were conducted by the dimethyl analogues-borate catalyst systems.

Half-titanocenes containing η²-pyrazolato ligands (coordinated to Ti in η²-N,N'-coordination mode) were prepared and their use as catalyst precursors for ethylene polymerisation in the presence of MAO were explored (Table 15).⁴⁰ The Cp^{*} analogues showed higher catalytic activities than the Cp analogues; Cp^{*}TiCl₂(C₃H₃N₂) exhibited the highest activity. In contrast to the results by the half-titanocenes containing the pyrrolide ligands, the resultant polymers possessed unimodal molecular weight

Table 13 Ethylene polymerisation by CpTi(CH₂Ph)₂(Y) (8)–co-catalyst systems^a

Y (anionic ligand)	Al co-cat.	Activity/kg-PE/mol-Ti·h bar	10 ⁻⁵ M _w ^b	M _w /M _n ^b
N=C[N(CH ₂) ₅] ₂	—	376	4.06	1.9
N=C[N(CH ₂) ₅] ₂	TIBAO	32	5.83	1.7
N=C[N(CH ₂) ₂ (2,6-Me ₂ C ₆ H ₃) ₂]	—	896	3.61	1.9
N=C[N(CH ₂) ₂ (2,6-Me ₂ C ₆ H ₃) ₂]	TIBAO	1600	6.63	2.2
N=C ⁱ Bu ₂	—	353	5.43	1.9
N=P ⁱ Bu ₃	—	848	5.18	2.2
N=P ⁱ Bu ₃	TIBAO	1128	7.17	2.1

^a Cited from ref. 27. *Conditions*: Ti 10 μmol, Al/B(C₆F₅)₃/Ti = 20/1.1/1.0 (molar ratio), ethylene 5 bar, 80 °C, 15 min, toluene 210 or 260 mL. ^b GPC data vs. polystyrene standards.

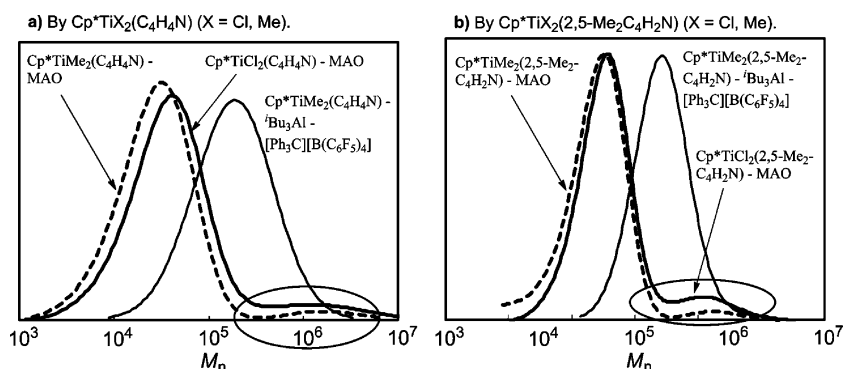


Fig. 2 GPC traces for resultant polyethylenes prepared by half-titanocenes containing pyrrolide ligands (data shown in Table 14).³⁹

Table 14 Ethylene polymerisation by Cp^{*}TiX₂(L) [Cp^{*} = Cp^{*}, Cp; L = C₄H₄N, 2,5-Me₂C₄H₂N; X = Cl, Me]–co-catalyst systems^a

Catalyst (μmol)	Activity ^b	10 ⁻³ M _n ^c	M _w /M _n ^c
Cp [*] TiCl ₂ (C ₄ H ₄ N) (0.2)	5550	22.7 ^d	2.38
Cp [*] TiCl ₂ (2,5-Me ₂ C ₄ H ₂ N) (0.2)	1500	20.7	2.38
Cp [*] TiMe ₂ (C ₄ H ₄ N) (0.2) ^e	10020	112	2.47
Cp [*] TiMe ₂ (C ₄ H ₄ N) (0.2)	5970	17.3 ^f	2.16
Cp [*] TiMe ₂ (2,5-Me ₂ C ₄ H ₂ N) (0.2) ^e	8100	160	2.75
Cp [*] TiMe ₂ (2,5-Me ₂ C ₄ H ₂ N) (0.2)	4620	12.6 ^f	2.88
CpTiCl ₂ (C ₄ H ₄ N) (0.2)	330	336	4.25
		2.18	2.23
CpTiCl ₂ (2,5-Me ₂ C ₄ H ₂ N) (0.2)	750	312	4.47
		2.61	2.12

^a Cited from ref. 39. *Conditions*: toluene total 30 mL, ethylene 6 atm, 10 min, 25 °C, d-MAO 3.0 mmol. ^b Activity = kg-PE/mol-Ti·h. ^c GPC data in *o*-dichlorobenzene vs. polystyrene standards. ^d Trace amount of high molecular weight polymer was also obtained in the GPC trace. ^e *Conditions*: [t-Bu₃Al]/[Ti] = 250, [[Ph₃C][B(C₆F₅)₄]]/[Ti] = 3.0. ^f Peak ascribed to high molecular weight was also seen in a trace amount.

Table 15 Ethylene polymerisation by Cp^{*}TiCl₂(Y) (10, Cp^{*} = Cp^{*}, Cp; Y = C₃H₃N₂, 3,5-Me₂C₃HN₂, 3,5-*i*-Pr₂C₃HN₂)–MAO catalyst systems^a

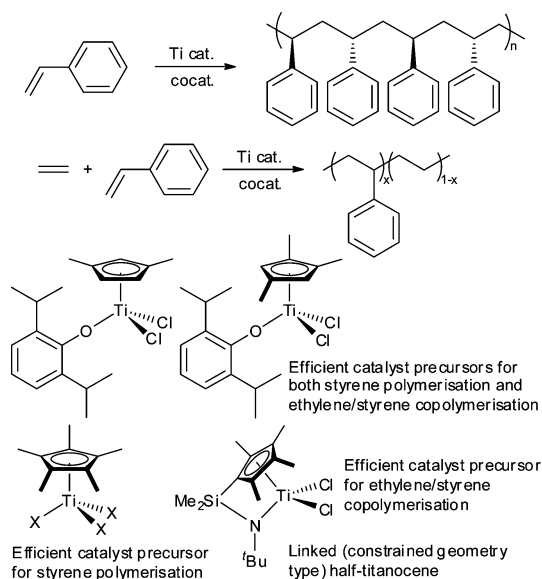
Catalyst Cp [*] , L	Activity ^b	10 ⁻⁴ M _n ^c	M _w /M _n ^c
Cp [*] , C ₃ H ₃ N ₂	9000	3.52	2.17
Cp [*] , 3,5-Me ₂ C ₃ HN ₂	7320	2.91	2.62
Cp [*] , 3,5- <i>i</i> -Pr ₂ C ₃ HN ₂	8700	2.40	2.44
Cp, C ₃ H ₃ N ₂	540	130.6	2.31
Cp, 3,5-Me ₂ C ₃ HN ₂	780	124.4	2.29
Cp, 3,5-Ph ₂ C ₃ HN ₂	1200	89.5	3.03

^a Cited from ref. 40. *Conditions*: complex 0.1 μmol, toluene total 30 mL, ethylene 6 atm, 10 min, 25 °C, d-MAO 2.0 mmol. ^b Activity = kg-PE/mol-Ti·h. ^c GPC data in *o*-dichlorobenzene vs. polystyrene standards. ^d Bimodal molecular weight distribution.

distributions in most cases.⁴⁰ The Cp analogues afforded ultra-high molecular weight polymers with unimodal distributions. These complexes were also effective for syndiospecific styrene polymerisation by the ligand modification,⁵³ both the Cp and ^tBuCp analogues were effective for the styrene polymerisation. More recently, we have demonstrated that (^tBuC₅H₄)TiCl₂(3,5-*i*-Pr₂C₃HN₂) exhibited better norbornene incorporation in the ethylene/norbornene copolymerisation. Precise tuning of both the Cp^{*} and the pyrrolato ligands were found to be very important for the desired polymerisation.

2. Syndiospecific styrene polymerisation and ethylene/styrene copolymerisation using half-titanocenes: ligand effects and some new mechanistic aspects

Syndiotactic polystyrene (SPS) is a unique polymeric material due to its high melting point (*T*_m = 270 °C), high crystallinity, low density, low dielectric constant, and high chemical resistance toward organic solvents.^{3,15a,41,54,55} This polymer cannot be prepared by free radical, anionic or ordinary Ziegler–Natta processes, but can be prepared by the syndiospecific polymerisation using various half-titanocenes (Scheme 4), Cp^{*}TiX₃ or Cp^{*}TiX₂(Y) (Cp^{*} = cyclopentadienyl group; X = halogen, alkoxo, alkyl, etc.; Y = anionic donor ligand).^{3,15a} Ethylene/styrene co-polymers, which cannot be prepared by conventional (free radical, Ziegler–Natta) processes,^{3,6b,15b,c,56} also attract considerable attention,⁵⁷ because styrene incorporation into the PE backbone results in drastic changes in the viscoelastic behavior as well as in the thermo-mechanical properties of the polymeric material.^{57b}



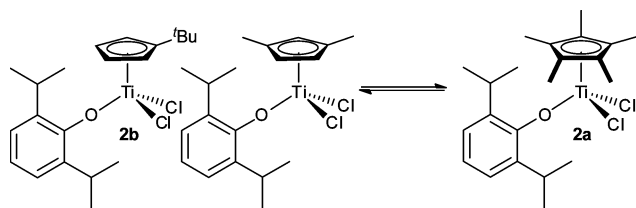
Scheme 4 Syndiospecific styrene polymerisation and ethylene/styrene copolymerisation by half-titanocenes.^{15b,c}

Half-titanocenes such as Cp^{*}TiF₃, Cp^{*}Ti(OMe)₃ and (indenyl)TiCl₃ are known to be efficient catalyst precursors for

syndiospecific styrene polymerisation.^{3,15a,41,54,55} However, these catalyst precursors showed low activities in the ethylene/styrene copolymerisation and the resultant polymers afforded a mixture of polyethylene, syndiotactic polystyrene and the copolymer.⁵⁸ In contrast, modified half-titanocenes of the type, Cp'TiX₂(Y), are effective not only for syndiospecific styrene polymerisation, but also for ethylene/styrene copolymerisation to afford the copolymers exclusively (Scheme 4).^{15b,c,32} Linked half-titanocenes (so-called "constrained geometry type") are also effective for ethylene/styrene copolymerisation,^{6,15b,c,59–62} although these complexes generally exhibited extremely low catalytic activities for styrene polymerisation.^{59a,62a} Certain metallocenes and group 4 transition metal complexes, so-called post-metallocenes are also known to be effective for the copolymerisation.^{63–66}

2.1. Effect of ligand in syndiospecific styrene polymerisation using Cp'TiX₂(Y)–MAO catalyst systems

Modified half-titanocenes, especially aryloxo modified half-titanocenes, showed unique characteristics in ethylene copolymerisations.^{7b,c,28–32} It was also demonstrated that an efficient catalyst for ethylene polymerisation can be modified for syndiospecific styrene polymerisation by ligand modification of the cyclopentadienyl fragment [Cp* analogue (**2a**), 1,3-Me₂C₅H₃ or ^tBuC₅H₄ (**2b**) analogues] (Scheme 5).^{15c,32a} Moreover, as described below, these complexes incorporate styrene efficiently in the ethylene/styrene copolymerisation affording the copolymers exclusively even with high styrene contents (>50–80 mol%).^{15b,c,32a,b} The role of the anionic donor ligand (aryloxo *etc.*) should be negligible according to an assumption that cationic Ti(III), [Cp'Ti(R)(styrene)]⁺ (R = polymer, alkyl chain) plays an essential role for the syndiospecific styrene polymerisation,^{54,55,67} but we explored the effect toward the activity in this catalysis.^{15c,24a,68–70}



Scheme 5 Ligand modifications for efficient catalysts.^{15b,c}

Table 16 summarises the results for styrene polymerisation using a series of Cp'TiCl₂(OAr) (Ar = 2,6-ⁱPr₂C₆H₃) and Cp'TiCl₃ [Cp' = Cp, 1,3-Me₂C₅H₃, 1,2,4-Me₃C₅H₂, C₅Me₅] complexes in the presence of MAO at various temperatures.⁶⁸ The activities by Cp'TiCl₂(OAr)–MAO catalyst system increased at higher temperature; the activity with 16000 kg-sPS/mol-Ti·h could thus be attained with CpTiCl₂(OAr) at 85 °C (Table 16). The observed activities by the aryloxo systems increased at high temperatures in most cases, and the activity at 70 °C increased in the order: Cp > 1,3-Me₂C₅H₃ ≫ 1,2,4-Me₃C₅H₂ > C₅Me₅. The trend was the same as that by the trichloride systems, suggesting that the activity was strongly affected by the nature of cyclopentadienyl fragment. The observed trend was similar to that reported by Kaminsky.^{54f} The *M_w* values in the resultant SPS prepared by the aryloxo analogue–MAO catalyst systems increased in the order: C₅Me₅

Table 16 Syndiospecific styrene polymerisation by Cp'TiCl₂(Y) [Y = Cl or OAr; Ar = 2,6-ⁱPr₂C₆H₃]-MAO catalyst systems^a

Cp'TiCl ₂ (Y)	T/°C	Activity ^b	10 ⁻⁴ <i>M_w</i> ^c	<i>M_w</i> / <i>M_n</i> ^c
CpTiCl ₂ (OAr)	40	1000	5.7	2.1
CpTiCl ₂ (OAr)	55	4130	5.8	2.0
CpTiCl ₂ (OAr)	70	15300	4.0	2.5
CpTiCl ₂ (OAr)	85	16000	2.2	2.4
(1,3-Me ₂ C ₅ H ₃)TiCl ₂ (OAr)	40	8460	35.2	2.3
(1,3-Me ₂ C ₅ H ₃)TiCl ₂ (OAr)	55	11500	18.2	2.0
(1,3-Me ₂ C ₅ H ₃)TiCl ₂ (OAr)	70	13700	8.6	1.9
(1,2,4-Me ₃ C ₅ H ₂)TiCl ₂ (OAr)	40	3680	35.4	2.1
(1,2,4-Me ₃ C ₅ H ₂)TiCl ₂ (OAr)	70	6900	12.5	1.7
Cp*TiCl ₂ (OAr)	40	285	26.8	2.6
Cp*TiCl ₂ (OAr)	55	1640	53.1	2.5
Cp*TiCl ₂ (OAr)	70	3600	49.0	2.2
Cp*TiCl ₂ (OAr)	85	4290	32.3	2.2
CpTiCl ₃	40	15800	6.7	2.8
CpTiCl ₃	55	17500	4.8	2.7
CpTiCl ₃	70	15300	3.3	2.4
CpTiCl ₃	85	13300	2.2	2.2
(1,3-Me ₂ C ₅ H ₃)TiCl ₃	40	6110	34.3	2.2
(1,3-Me ₂ C ₅ H ₃)TiCl ₃	55	9510	17.6	2.0
(1,3-Me ₂ C ₅ H ₃)TiCl ₃	70	7270	10.3	2.1
(1,2,4-Me ₃ C ₅ H ₂)TiCl ₃	40	1650	16.1	1.7
(1,2,4-Me ₃ C ₅ H ₂)TiCl ₃	70	3730	9.7	2.0
Cp*TiCl ₃	40	320	36.2	2.3
Cp*TiCl ₃	55	666	33.2	2.3
Cp*TiCl ₃	70	1970	24.8	2.5
Cp*TiCl ₃	85	3280	17.5	2.2

^a Cited from ref. 68. *Conditions*: complex 2.0 μmol, styrene/toluene = 10/20 mL, MAO white solid (Al/Ti = 1500, molar ratio), 10 min. ^b Activity in kg-sPS/mol-Ti·h. ^c GPC data in *o*-dichlorobenzene vs. polystyrene standards.

> 1,2,4-Me₃C₅H₂, 1,3-Me₂C₅H₃ > Cp. Although some *M_w* values by the aryloxo systems were different from those by the trichloride systems, the order in the *M_w* values was very similar to that by the trichloride systems;⁶⁸ it thus seems that the introduction of an electron-donating substituent on the Cp' was effective in obtaining high molecular weight SPS under these conditions (probably due to the enhanced propagation rate by introducing an electron-donating group on the Cp', or as a result of the difference in the chain-transfer step by introducing steric bulk on Cp').⁶⁸

The results using the Cp*TiCl₂(Y) (varying a series of anionic donor ligands) in the presence of MAO co-catalyst are summarised in Table 17.^{15c,24a,68–70} Cp*TiCl₂(O-2,6-Me₂C₆H₃) exhibited remarkable activities which increased at higher temperature.⁶⁸ The activity at 70 °C increased in the order: Y = O-2,6-Me₂C₆H₃ ≫ OPh, O-4-MeC₆H₄, O-2,6-ⁱPr₂C₆H₃ > Cl, O-2,6-ⁱBu₂C₆H₃ > O-2-Me-6-(ArN=CH)C₆H₃ > O-2-ⁱBu-6-(ArN=CH)C₆H₃ > N=C'Bu₂. The results clearly indicate that the substituent on the aryloxo (anionic donor) ligand *directly affects* the catalytic activity. Moreover, the *M_w* value for resultant SPS was also dependent upon the anionic ligand employed. These results suggest that aryloxo ligand play an important role toward both the activity and the *M_w* value.

The activities in the styrene polymerisation using a series of (^tBuC₅H₄)TiCl₂(Y) were also dependent upon the aryloxo ligand employed, and the activity increased in the order (conditions: complex 1.0 μmol, Al/Ti = 3000, 25 °C, 10 min): Y = O-2,6-ⁱPr₂-4-ⁱBuC₆H₂ (2680 kg-sPS/mol-Ti·h) > O-2,6-Me₂C₆H₃, O-2,6-ⁱPr₂C₆H₃ (1370) > O-2,4,6-Me₃C₆H₂ (534) > O-2,6-ⁱBu₂C₆H₃ (258) > O-2,6-ⁱBu₂-4-MeC₆H₂ (54).⁴⁴ Moreover, the activity by (1,3-Me₂C₅H₃)TiCl₂(Y), [Y = Cl, O-2,6-ⁱPr₂C₆H₃,

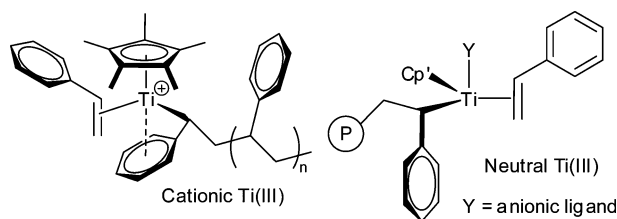
Table 17 Effect of anionic donor ligand in styrene polymerisation by Cp*TiCl₂(Y)–MAO catalyst systems^a

Y (anionic ligand)	T/°C	Activity ^b	10 ⁻⁴ M _w ^c	M _w /M _n ^c
Cl	40	320	36.2	2.3
Cl	70	1970	24.8	2.5
Cl	85	3280	17.5	2.2
OC ₆ H ₅	40	733	55.1	2.2
OC ₆ H ₅	70	4170	54.3	2.0
OC ₆ H ₅	85	6390	47.8	2.1
O-4-MeC ₆ H ₄	40	757	30.4	2.8
O-4-MeC ₆ H ₄	70	3750	26.7	2.4
O-4-MeC ₆ H ₄	85	6020	24.2	2.3
O-2,6-Me ₂ C ₆ H ₃	40	1020	30.1	2.3
O-2,6-Me ₂ C ₆ H ₃	70	9200	28.0	2.1
O-2,6-Me ₂ C ₆ H ₃	85	12400	20.7	2.1
O-2,6-Pr ₂ C ₆ H ₃	40	285	26.8	2.6
O-2,6-Pr ₂ C ₆ H ₃	70	3600	49.0	2.2
O-2,6-Pr ₂ C ₆ H ₃	85	4290	32.3	2.2
O-2,6-t-Bu ₂ C ₆ H ₃	40	75	11.0	1.9
O-2,6-t-Bu ₂ C ₆ H ₃	70	1780	20.5	2.3
O-2,6-t-Bu ₂ C ₆ H ₃	85	5690	23.1	2.2
O-2-Me-6-(ArN=CH)C ₆ H ₃	40	192	21.3	2.1
O-2-Me-6-(ArN=CH)C ₆ H ₃	70	552	18.5	2.3
O-2-t-Bu-6-(ArN=CH)C ₆ H ₃	40	126	19.3	2.3
O-2-t-Bu-6-(ArN=CH)C ₆ H ₃	70	378	17.1	2.2
N=C ⁻ Bu ₂	40	81	20.9	2.3
N=C ⁻ Bu ₂	70	222	19.1	2.1

^a Cited from refs. 24a and 68–70. Conditions: complex 2.0 μmol, styrene/toluene = 10/20 mL, MAO white solid (Al/Ti = 1500, molar ratio), 10 min. ^b Activity in kg-sPS/mol-Ti-h. ^c GPC data in *o*-dichlorobenzene vs. polystyrene standard.

N(Me)Cy (Cy = cyclohexyl), N(2,6-Me₂C₆H₃)(SiMe₃)–MAO catalyst systems strongly depended upon the anionic donor ligand employed,⁶⁸ and use of aryloxo ligand was effective for exhibiting the high activity, and molecular weight distribution for SPS prepared by the anilide analogue was bimodal, probably due to generation of the several catalytically-active species being present in the reaction mixture.⁶⁸ These results also suggested that the role of anionic ligand is present in this catalytic polymerisation.

As described above, ordinary half-titanocenes such as Cp*TiCl₃, Cp*Ti(OMe)₃, (indenyl)TiCl₃ are known to be efficient catalyst precursors for syndiospecific styrene polymerisation in the presence of a co-catalyst.^{3,15a,41,54,55,67} The oxidation state of the active species has been invoked as cationic Ti(III) (Scheme 6 left),^{54,55,57} whereas the cationic Ti(IV) species would play a role for the ethylene/styrene copolymerisation.^{15b,32d,e,58} In contrast, Tomotsu (Idemitsu) insisted a possibility that neutral Ti(III) species,^{54g} [Cp'Ti(R)(Y)(styrene)] (Y = anionic ligand), should play a role as the active species (Scheme 6 right).^{3,15}

**Scheme 6** Proposed catalytically-active species for syndiospecific styrene polymerisation.^{13a-c}**Table 18** Ethylene/styrene copolymerisation using Cp*Ti(CH₂Ph)₃–B(C₆F₅)₃–AlⁱBu₃ catalyst system^a

T/°C	Styrene/mol L ⁻¹	Yield ^b /g	Activity ^c	Composition ^d (wt%)		
				PE	E/S	SPS
0	1.1	0.30	48	> 90		
25	0.8	0.45	72	63	22	15
50	0.4	0.35	56	33	58	9
50	0.65	0.53	85	12	63	25
50	1.2	0.49	78	6	72	22
50	2.0	1.00	160	8	20	72
75	0.5	0.35	56	29	41	30

^a Cited from ref. 58b. Conditions: Cp*Ti(CH₂Ph)₃/B(C₆F₅)₃/AlⁱBu₃ = 25/25/25 μmol, ethylene 1 atm, toluene + styrene total 26 mL.

^b After removal of atactic polystyrene. ^c Activity in kg-polymer/mol-Ti-h.

^d Estimated from ¹³C NMR spectra.

On the basis of the above results, it is clear that both cyclopentadienyl fragment and anionic ancillary donor ligand play an essential role for exhibiting high activity as well as for affording high molecular weight syndiotactic polymer with unimodal molecular weight distribution. Since the role of anionic donor ligand toward both the activity and the molecular weight is present, if the possibility that neutral Ti(III) or cationic Ti(IV) species plays a role for this polymerisation, although it has been generally invoked that cationic Ti(III) plays an essential role for the syndiospecific styrene polymerisation.

2.2. Ethylene/styrene copolymerisation using half-titanocenes

As described above, half-titanocenes, Cp*TiX₃ (X = F, OMe *etc.*), which are efficient catalyst precursors for syndiospecific styrene polymerisation,^{3,15a,41,54,55} afforded a mixture of polyethylene (PE), syndiotactic polystyrene (SPS) and the copolymer (E/S copolymer) in the ethylene/styrene (co)polymerisation.^{58,32d} The product distribution and the activity in (co)polymerisation using a CpTiX₃–MAO catalyst system is thus highly sensitive to the anionic donor ligand (X = Cl, CH₂Ph, OCH₃, OCH₂Ph *etc.*), the reaction conditions, the nature of MAO,^{58c,d} and the exact mixing sequence and pre-contact time. These factors usually lead to poor reproducibility.

Pellecchia and Zambelli reported that Cp*Ti(CH₂Ph)₃–B(C₆F₅)₃ afforded E/S copolymer including PE and SPS, and the distributions were dependent upon the polymerisation temperature, the pretreatment procedure (Table 18).^{58b} The resultant copolymer possessed an alternating sequence, and no resonances ascribed to styrene repeating units were seen. However, it seems very difficult to find suitable conditions for the exclusive preparation of E/S copolymer (Table 18), and selective co-oligomerization proceeded in the presence of Cp'TiCl₃ (Cp' = Cp, Cp*, indenyl)–B(C₆F₅)₃ (MAO) catalyst systems under certain conditions.⁷¹

2.2.1. Recent results in ethylene/styrene copolymerisation by linked (constrained geometry type) half-titanocenes. Linked half-titanocenes are known to be efficient catalyst precursors for the copolymerisation,^{6,59–61} although they exhibited extremely low activity for the syndiospecific styrene polymerisation.^{59a,62a} It has also been reported that styrene incorporation by linked Cp-amide Ti catalyst (constrained geometry catalyst, CGC) systems

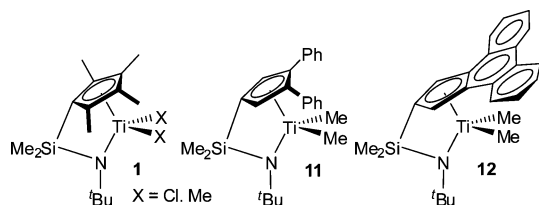
Table 19 Copolymerisation of ethylene with styrene using different linked half-titanocene–MAO catalyst systems^a

Complex	Activity ^b	10 ⁻⁴ M _w ^c	M _w /M _n ^c	Styrene ^d (mol%)
1 (X = Me)	23700	1.13	2.36	11.0
11	61000	7.28	4.76	21.5
12	99400	13.4	5.26	30.6

^a Cited from ref. 59c. *Conditions*: complex 3.0 μmol, styrene 455 g, toluene 433 g, ethylene 200 psi (13.6 atm), H₂ 50 psi, B(C₆F₅)₃ 3.0 μmol, 90 °C, 30 min. ^b Activity in kg-polymer/mol-Ti·h. ^c GPC data vs. polyethylene standards. ^d Styrene content in E/S copolymer estimated by ¹H NMR spectra.

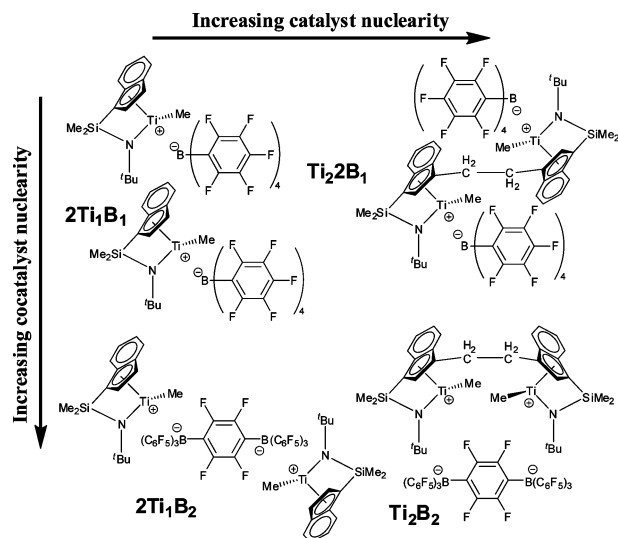
is invariably <50 mol%, regardless of the styrene/ethylene feed ratio.^{6,59–61}

It has been known that the cyclopentadienyl fragment affected both the catalytic activity and the styrene incorporation,⁶⁰ and substitution of an amide ligand was also effective for improving the styrene incorporation:^{61b,c} notable styrene incorporation was seen with the cyclohexyl analogue, [Me₂Si(C₅Me₄)(NCy)]TiCl₂, although a decrease in the activity was observed.^{61c} Klosin and Timmers *et al.* (Dow Chemicals) reported that complexes **11** and **12** (Scheme 7) show a significantly better efficiency and styrene reactivity than catalyst **1** (X = Me) (Table 19).^{59c} Complex **11** was less efficient and less reactive toward styrene than **12** under the same conditions, and this may be due not only to the steric bulk of the freely rotating phenyl groups, but also to electronic effects, where more effective electron donors to the Cp fragment through conjugation should be possible in the permanently coplanar aryl groups of **12**.^{59c}

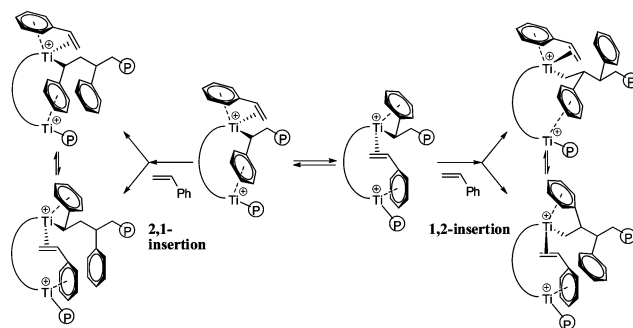
**Scheme 7** Selective set of linked half-titanocenes employed for ethylene/styrene copolymerisation.⁵⁹

As described above, mononuclear linked half-titanocenes (constrained geometry catalysts, CGCs) showed extremely low catalytic activity for styrene polymerisation, and the styrene content in the resultant copolymer did not exceed 50 mol%. In contrast, the bimetallic system (**Ti₂B₁** or **Ti₂B₂** in Scheme 8) recently reported by Marks *et al.* exhibited significantly higher catalytic activities for styrene polymerisation than the mononuclear system (**2Ti₁B₁** or **2Ti₁B₂**), although the resultant polymer possessed *atactic* stereoregularity (Table 20).⁶² The resultant polystyrene possessed unimodal GPC traces (M_w/M_n = 1.44, 1.47), and an end group analysis results showed that homopolymers are produced exclusively *via* a coordination/insertion pathway.

Efficiency in the styrene incorporation in the ethylene/styrene copolymerisation dramatically improved with the use of a dinuclear catalyst system (**Ti₂B₁**); synthesis of a copolymer with a high styrene content (76 mol%) has thus been achieved in this catalysis (Table 20). Therefore, this catalyst system afforded broad-range controllable styrene incorporation (styrene contents 39–76 mol%) in the copolymerisation, although the observed activities

**Scheme 8** Catalyst/co-catalyst nuclearity matrix for constrained geometry catalysts.^{62b}

should be further improved.^{62a} Resonances ascribed to the three consecutive head-to-tail coupled styrene units in addition to tail-to-tail coupled dyads were observed in the ¹³C NMR spectra of the resultant copolymers (styrene >50 mol%).^{62a} It was assumed that the arene ring of the last-inserted styrene may preferentially coordinate to the adjacent Ti center in the bimetallic **Ti₂** (Scheme 9), thus reducing coordinative saturation at the polymerisation site and accelerating homopolymerisation.^{62a,b} The coordinated arene rings can, in principle, participate in several types of multimetallic/enchainment-altering interaction.

**Scheme 9** Proposed pathways in the ethylene/styrene copolymerisation.^{62b}

2.2.2. Ethylene/styrene copolymerisation by modified half-titanocenes, Cp⁺TiX₂(Y). The aryloxo modified half-titanocenes, Cp⁺TiX₂(O-2,6-*i*-Pr₂C₆H₃) (Cp⁺ = cyclopentadienyl group; X = Cl, Me) exhibited high catalytic activities for ethylene/styrene copolymerisation in the presence of MAO, affording poly(ethylene-co-styrene)s exclusively without PE and/or SPS as by-products (Table 21).^{32a,b} The resultant copolymers possessed not only relatively high molecular weights with unimodal molecular weight distributions, but also single composition as confirmed by DSC thermograms, CFC and GPC/FT-IR.^{32b} The activities decreased slightly with an increase in the styrene concentration, whereas the styrene contents in the copolymers increased upon increasing the [S]/[E]

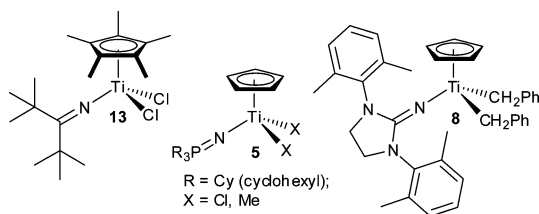
Table 20 Styrene polymerisation and ethylene/styrene copolymerisation catalysed by mononuclear or dinuclear linked half-titanocenes-co-catalyst systems^a

Cat.	Styrene/toluene (mL)	Ethylene/atm	t/h	Activity ^b	10 ⁻⁴ M _w ^c	M _w /M _n ^c	Styrene ^d (mol%)
Ti ₁ + B ₁	5/25	—	3	2.7	11.96	1.84	100
Ti ₂ + B ₂	5/25	—	3	104	1.04	1.44	100
Ti ₂ + B ₁	5/25	—	3	112	0.80	1.47	100
Ti ₂ + B ₁	10/50	1.0	1	259	35.8	1.82	39
Ti ₂ + B ₁	20/40	1.0	1.5	194	47.1	1.33	50
Ti ₂ + B ₁	30/30	1.0	0.5	384	43.8	2.40	66
Ti ₂ + B ₁	60/0	1.0	0.5	312	47.9	1.72	76

^a Cited from ref. 62. **Conditions:** Ti₁ (10 μmol) or Ti₂ (5 μmol) + B₁ (10 μmol) or B₂ (5 μmol), 20 °C, ethylene 1.0 atm. ^b Activity in kg-polymer/mol-Ti-h. ^c By DSC thermograms. ^d GPC data vs. polystyrene standards. ^e Estimated by ¹³C NMR spectra.

initial feed molar ratios. Styrene incorporations with aryloxo analogues is more efficient than that with [Me₂Si(C₅Me₄)(NⁱBu)]TiCl₂ (**1**, X = Cl). Thus, the present catalysis provides an efficient synthesis of copolymer with high styrene content, especially higher than 50 mol%, in a random manner. The analysis of the microstructure of the resultant E/S copolymers by ¹³C NMR spectroscopy indicated that the resultant copolymer prepared by the 1,2,3-Me₃C₅H₂ analogue, (1,2,3-Me₃C₅H₂)TiCl₂(O-2,6-ⁱPr₂C₆H₃), possesses resonances ascribed to two or three styrene repeat units connected *via* head-to-tail coupling, in addition to the resonances ascribed to tail-to-tail coupling of a styrene unit or head-to-head bridged by an intervening ethylene unit. This is especially interesting in contrast to the results with the linked half-titanocene (**1**).^{15a,32a,b}

Copolymerisation by other modified half-titanocenes has also been reported (Scheme 10). Ethylene/styrene copolymerisation by Cp*TiCl₂(N=CⁱBu₂) (**13**) took place in a living manner in the presence of MAO co-catalyst, although the homopolymerisation of ethylene and styrene did not proceed in a living manner.^{32c} No styrene repeating units were observed in the resultant copolymers, suggesting that a certain degree of styrene insertion inhibits chain transfer in this catalysis. The living nature was maintained under various conditions (Al/Ti molar ratios, ethylene pressure, styrene concentrations, temperature).^{32d}



Scheme 10 Other modified half-titanocenes employed for the ethylene/styrene copolymerisation.^{26b,27,32c,d}

Copolymerisation with CpTiX₂(N=PCy₃) (**5**, X = Cl, Me)-co-catalyst (MAO, borates) systems proceeded with notable catalytic activities [at 60–90 °C, ethylene 70 psi (4.76 atm), [S]/[E] = 12],^{26b} however, styrene incorporation seemed less efficient than with either aryloxo analogues or linked half-titanocene [styrene content: 33.4–61.4 wt% (<27.6 mol%)].^{26b,72} Half-titanocene containing iminoimidazolidide ligand (**8**) also exhibited remarkable catalytic activity under certain conditions, but the styrene content in the resultant copolymer was low [ethylene 5 bar, styrene/toluene = 20/210 mL, 80 °C; activity = 1960 kg-polymer/mol-Ti-h, M_w = 1.79 × 10⁵, M_w/M_n = 2.1, styrene 10 wt% (2.9 mol%)].²⁷

Taking into account the above results, it is clear that modified half-titanocenes, Cp*TiX₂(Y), are better catalyst precursors for synthesis of ethylene/styrene copolymers in high yields. It was also clear that both the activity and the styrene incorporation are dependent upon the type of ligands employed (cyclopentadienyl fragment and anionic donor ligand). These complexes are also effective for not only ethylene polymerisation, but also syndiospecific styrene polymerisation; the results are in unique contrast to those with ordinary half-titanocenes, Cp*TiX₃. Therefore, these catalysts may be suitable for mechanistic study on syndiospecific styrene polymerisation as well as copolymerisation, as described below.^{15b,32d,e}

2.3. Role of anionic donor ligand in ethylene/styrene copolymerisation and syndiospecific styrene polymerisation: Mechanistic considerations

Ethylene/styrene copolymerisations using three half-titanocenes containing Cp* ligand of type, Cp*TiX₂(Y) [X = Cl, Y = N=CⁱBu₂, O-2,6-ⁱPr₂C₆H₃, Cl; X = Me, Y = O-2,6-ⁱPr₂C₆H₃, Me]-co-catalyst systems were used under the same conditions (Table 22 and Table 23).^{32d} In copolymerisation using the Cp*-ketimide analogue (**13**)-MAO catalyst, both the activities and the styrene content increased at higher temperature. The resultant copolymers prepared with the ketimide analogue even at 55 °C still possessed relatively low PDI values, suggesting that the living nature was maintained under these conditions. The polymerisations with the aryloxo analogue, Cp*TiCl₂(OAr) (**2a**), gave copolymers with high styrene contents (31.9–34.3 mol%), and significant increase in the activity was not observed at high temperature. The resultant copolymers prepared by **2a** possessed lower M_n values with unimodal, rather large PDI values (M_w/M_n = 1.50–1.62) than those prepared by the Cp*-ketimide analogue, suggesting that a chain-transfer reaction occurred to certain degree. In contrast, the polymers prepared with the trichloride analogue, Cp*TiCl₃, showed bimodal molecular weight distributions consisting of a mixture of PE and SPS, and the proportion of SPS increased at high temperature due to an increase in the activity for syndiospecific styrene polymerisation.^{32b,68}

Copolymerisation using the aryloxy-dimethyl analogue, Cp*TiMe₂(OAr)-MAO or [PhN(H)Me₂][B(C₆F₅)₄] (AFPB) catalyst system afforded the copolymer (Table 23);^{32d} no distinct differences in the microstructures were observed in the ¹³C NMR spectra. In contrast, the polymer prepared with the Cp*TiMe₂-AFPB catalyst was PE (containing a trace amount of the

Table 21 Ethylene/styrene copolymerisation by Cp*TiCl₂(OAr) [Cp* = 1,2,3-Me₃C₃H₂, 1,3-Me₂C₃H₃, ⁱBuC₃H₄; OAr = O-2,6-ⁱPr₂C₆H₃] or [Me₂Si(C₂Me₂)(NⁱBu)]TiCl₂-MAO catalyst systems^a

Complex	Styrene/mL	Activity ^b	Content ^c (wt%)	E/S Copolymer (THF soluble)		
				10 ⁻⁴ M _w ^d	M _w /M _n ^d	Styrene ^e (mol%)
(1,2,3-Me ₃ C ₃ H ₂)TiCl ₂ (OAr)	3	4100	99.1	17.0	1.6	26.0
(1,2,3-Me ₃ C ₃ H ₂)TiCl ₂ (OAr)	5	3070	98.3	11.0	1.7	38.8
(1,2,3-Me ₃ C ₃ H ₂)TiCl ₂ (OAr)	10	2720	97.8	6.6	1.6	51.2
(1,2,3-Me ₃ C ₃ H ₂)TiCl ₂ (OAr) ^f	15	1850	90.4	3.6	2.1	73.6
(1,3-Me ₂ C ₃ H ₃)TiCl ₂ (OAr)	10	4140	98.2	3.7	1.6	49.0
(ⁱ BuC ₃ H ₄)TiCl ₂ (OAr)	10	1840	98.7	3.5	2.2	51.2
[Me ₂ Si(C ₂ Me ₂)(N ⁱ Bu)]TiCl ₂	10	5630	99.6	18.0	1.8	32.7

^a Cited from ref. 32b. *Conditions*: complex 1.0 μmol (2.0 μmol mL⁻¹-toluene), ethylene 4 atm, total volume of toluene and styrene = 30 mL, MAO white solid (Al/Ti = 2000, molar ratio), 25 °C, 10 min. ^b Activity (kg-polymer/mol-Ti-h), polymer yield in acetone insoluble fraction. ^c Percentage of content in copolymer based on polymer obtained (acetone insoluble, THF soluble fraction). ^d GPC data in *o*-dichlorobenzene vs. polystyrene standards. ^e Styrene content (mol%) in copolymer by ¹H NMR (1,1,2,2-C₂D₂Cl₄). ^f Conducted under ethylene 2 atm.

Table 22 Copolymerisation of ethylene with styrene by Cp*TiCl₂(Y) [Y = N=CⁱBu₂, O-2,6-ⁱPr₂C₆H₃, (OAr), Cl]ⁱ-MAO catalyst systems^a

Cat. Y	T/°C	Composition ^b (%)			Activity ^c	Styrene ^d (mol%)	10 ⁻⁴ M _n ^e	M _w /M _n ^e
		E-S	PE	SPS				
N=C ⁱ Bu ₂	25	> 99	<i>tr.</i>	<i>tr.</i>	396	7.4	9.5	1.18
N=C ⁱ Bu ₂	40	> 99	<i>tr.</i>	<i>tr.</i>	790	9.3	14.4	1.28
N=C ⁱ Bu ₂	55	> 99	<i>tr.</i>	<i>tr.</i>	1110	10.4	19.7	1.31
OAr	25	> 99	<i>tr.</i>	<i>tr.</i>	504	31.9	9.28	1.62
OAr	40	> 98	<i>tr.</i>	<i>tr.</i>	660	34.3	9.79	1.50
Cl ⁱ	25	<i>tr.</i>	86.8	13.2	250	> 99 ^g	5.85	1.26
						—	0.29	2.69
Cl ⁱ	40	<i>tr.</i>	81.6	18.4	280	> 99 ^g	5.07	1.31
						—	0.31	1.75
Cl ⁱ	55	<i>tr.</i>	69.8	30.2	260	> 99 ^g	3.56	1.48
						—	0.21	1.77

^a Cited from ref. 32d. *Conditions*: catalyst 2.0 μmol, MAO white solid 3.0 mmol, ethylene 6 atm, styrene 10 mL, styrene + toluene total 30 mL, 10 min. ^b Based on a mixture of PE, SPS and copolymer. (acetone insoluble fraction). ^c Activity in kg-polymer/mol-Ti-h. ^d Styrene content (mol%) estimated by ¹H NMR spectra. ^e GPC data in *o*-dichlorobenzene vs. polystyrene standards. ^f Resultant polymers were a mixture of PE and SPS. ^g Confirmed by GPC/FT-IR, ¹³C NMR spectra, DSC thermograms.

copolymer with low styrene content) or the copolymer with an extremely low styrene content, whereas the copolymerisation in the presence of MAO afforded a mixture of PE and SPS, as observed in the (co)polymerisation using Cp*TiCl₃. The fact that no SPS was formed in polymerisation with Cp*TiMe₃-AFPB catalyst was analogous to the fact that Cp*Ti(CH₂Ph)₃-AFPB catalyst did not afford SPS in an attempted styrene polymerisation (under dark conditions), and only poly(propylene-co-styrene) oligomer was formed in the propylene/styrene copolymerisation.⁶⁷

These results strongly suggest that cationic Ti(IV) species play an important key role in the ethylene polymerisation as well as the ethylene/styrene copolymerisation. These results also suggest that another catalytically-active species [likely Ti(III)] for syndiospecific styrene polymerisation is formed in the presence of MAO.^{32d}

Exclusive formation of copolymers without formation of SPS as a by-product was observed with the introduction of ethylene into a solution of syndiospecific styrene polymerisation using

Table 23 Ethylene/styrene copolymerisation by Cp*TiMe₂(O-2,6-ⁱPr₂C₆H₃), Cp*TiMe₃-MAO or [PhN(H)Me₂][B(C₆F₅)₄] (AFPB) catalyst systems^a

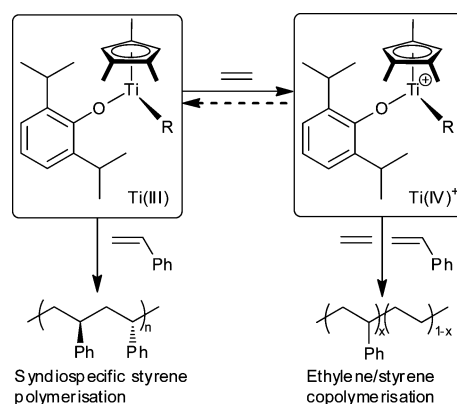
Cat. (μmol)	t/min	Composition ^b (%)			Activity ^c	Styrene ^d (mol%)	10 ⁻⁴ M _n ^e	M _w /M _n ^e
		E-S	PE	SPS				
Cp*TiMe ₂ (OAr)/MAO (2.0)	10	99	<i>tr.</i>	<i>tr.</i>	519	30.5	5.34	2.05
Cp*TiMe ₂ (OAr)/AFPB (5.0)	20	99	<i>tr.</i>	<i>tr.</i>	79.2	46.7	2.81	2.16
Cp*TiMe ₃ /MAO (2.0)	10	<i>tr.</i>	68.6	31.4	366	> 99	8.66	1.37
						—	0.81	2.33
Cp*TiMe ₃ /AFPB (10.0)	20	<i>tr.</i>	99	<i>tr.</i>	43.8	<i>tr.</i>	0.5	3.53

^a Cited from ref. 32d. *Conditions*: catalyst 2.0 μmol, MAO 3.0 mmol or AlⁱBu₃ 1.0 mmol (borate system), [C₆H₅NH(Me)₂][B(C₆F₅)₄] (AFPB) 2.0 μmol, styrene 10.0 mL, toluene 20 mL, 10 min. ^b Based on a mixture of PE, SPS and copolymer. (acetone insoluble fraction). ^c Activity in kg-polymer/mol-Ti-h. ^d Styrene content (mol%) estimated by ¹H NMR spectra. ^e GPC data in *o*-dichlorobenzene vs. polystyrene standards. *tr.* = trace.

$\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ ($\text{Cp}^* = i\text{BuC}_5\text{H}_4, 1,2,4\text{-Me}_3\text{C}_5\text{H}_2$)–MAO catalysts (Scheme 11). Note that the activities and the M_w values as well as the styrene contents in the latter copolymerisations were identical to those in their independent runs. These results clearly indicate that the active species for the syndiospecific styrene polymerisation can be tuned to the active species for copolymerisation.^{32e,73} In contrast, styrene polymerisation did not proceed when ethylene was removed from the reaction mixture of ethylene/styrene copolymerisation (likely due to oxidation upon exposure to ethylene).^{32e}

Taking into account the facts in addition to those in Table 23,^{32d} the cationic Ti(IV) species, $[\text{Cp}^*\text{Ti}(\text{L})\text{R}]^+$, likely play a role in the copolymerisation and the active species containing an anionic ancillary donor ligand [assumed to be neutral Ti(III), $\text{Cp}^*\text{Ti}(\text{L})\text{R}$] proposed by Tomotsu *et al.*^{54g} plays a role in syndiospecific styrene polymerisation (Scheme 12).^{32e} These results should also explain the reported findings that the catalytic activities and molecular weight of the resultant syndiotactic polystyrene in styrene polymerisation using $\text{Cp}^*\text{TiX}_2(\text{Y})$ -co-catalyst systems were highly dependent upon the anionic donor ligand (Y), regardless of kind of the co-catalyst used.^{32d,e,73} These proposals are in contrast to the hypothesis that cationic Ti(III) species, $[\text{Cp}^*\text{Ti}(\text{R})(\text{styrene})]^+$, play a role as the catalytically-active species for the styrene polymerisation using Cp^*TiX_3 . This hypothesis should help to explain why polystyrene structures in the resultant copolymers prepared with $\text{Cp}^*\text{TiCl}_2(\text{Y})$ -MAO catalysts are atactic.

Promising results have been reported regarding copolymerisation using linked (so-called “constrained geometry type”) half-titanocenes and modified half-titanocenes $[\text{Cp}^*\text{TiX}_2(\text{Y})]$, affording random copolymer with various styrene contents, and both the catalytic activities and the styrene incorporation are highly affected by both the cyclopentadienyl fragments and anionic donor ligands employed. The efficient synthesis of random copolymers could be achieved by using half-titanocenes containing aryloxy ligands. Cationic Ti(IV) species play an important role as catalytically-active species in copolymerisation, whereas (neutral and/or cationic) Ti(III) species play roles in syndiospecific styrene polymerisation, and these findings may suggest why the



Scheme 12 Proposed catalytically-active species for syndiospecific styrene polymerisation and ethylene/styrene copolymerisation.^{15b,32d}

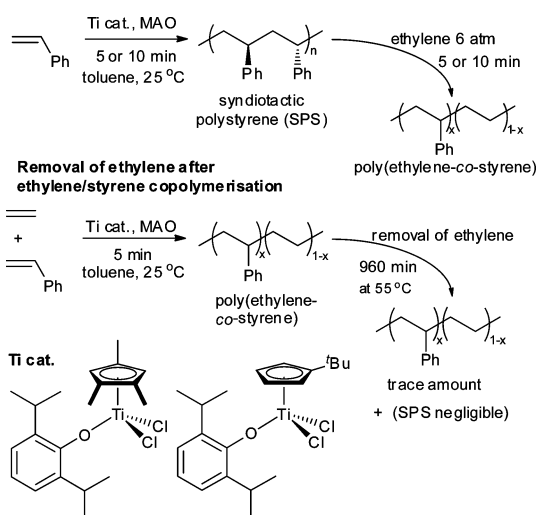
polystyrene structure in random copolymer prepared with half-titanocenes was atactic.

Conclusion

As presented in this perspective article, it is now clear that *nonbridged* modified half-titanocenes containing anionic ancillary donor ligand of the type, $\text{Cp}^*\text{TiX}_2(\text{Y})$, displayed unique characteristics that are different from those especially of ordinary catalysts (Ziegler–Natta, metallocenes, linked half-titanocenes). Modifications of both the cyclopentadienyl fragment (Cp^*) and anionic donor ligands (Y) are very important especially for the successful copolymerisations (with both remarkable activities and efficient comonomer incorporation).^{7b,c} As demonstrated in the aryloxy,^{32a} amide⁶⁹ and phenoxyimine⁷⁰ analogues in this article, the efficient catalyst precursors for ethylene polymerisation can be tuned to the efficient catalyst precursors for syndiospecific styrene polymerisation by simple modification of cyclopentadienyl fragment; we believe that this is one of the unique characteristics for using this catalysis. Fine tuning of anionic donor ligand is also important for exhibiting high catalytic activity (with better stability in the catalytic reaction) as well as with better comonomer incorporation.

We could see many reports concerning syntheses of half-titanocenes of this type and their potential as ethylene polymerisation catalysts. However, unfortunately, we could not see the details in most cases; many researchers stopped their evaluations only by ethylene polymerisation. As described here, we need more information concerning the catalyst stability in the reaction mixture, electronic and steric effects toward both the activity and the comonomer incorporation for their further fine tuning. Since we now realize that the complexes of type should be effective for synthesis of new polyolefins by incorporation of monomers that are not successful in ordinary catalysts, these studies should be thus explored in the near future.

Several promising findings that should be very important from both academic and industrial viewpoints have been demonstrated. These efforts will pave new promising possibilities for evolution of new *fine* polyolefins with unique properties by incorporation of new comonomers and/or by adopting new synthetic strategies.



Scheme 11 Step (co)polymerisation of ethylene with styrene.^{32d}

Acknowledgements

K. N. expresses his heartfelt thanks to former group members who contributed this project as coauthors. K. N. also express his sincere thanks to many researchers, especially to Dr Bart Hessen, Prof. Moris S. Eisen (Technion, Israel Institute of Technology) and to Dr Norio Tomotsu (Idemitsu Kosan, Co. Ltd.) for helpful discussions concerning mechanistic considerations in syndiospecific styrene polymerisation and ethylene/styrene copolymerisation. We also thank to Prof. Jingyao Liu (Jilin Univ.) for her kind help in preparing the manuscript. This research was partly supported by Grant-in-Aid for Scientific Research (B) from the Japan Society for the Promotion of Science (JSPS, No. 18350055, No. 21350054). K. N. thanks Tosoh Finechem Co. for donating MAO.

References

- 1 For example, (a) A. H. Tullo, *Chem. Eng. News*, 2008, **86**(40), 24–25; (b) Plastics Europe website, <http://www.plasticseurope.co.uk/>; (c) V. Busico, *Dalton Trans.*, 2009, 8794.
- 2 Reviews for cyclic olefin copolymers, see: (a) W. Kaminsky, *Angew. Makromol. Chem.*, 1994, **223**, 101; (b) H. Cherdron, M.-J. Brekner and F. Osan, *Angew. Makromol. Chem.*, 1994, **223**, 121; (c) W. Kaminsky, I. Beulich and M. Arndt-Rosenau, *Macromol. Symp.*, 2001, **173**, 211; (d) V. Dragutan, and R. Streck, *Catalytic Polymerisation of Cycloolefins*, Studies in Surface Science and Catalysis, vol 131, Elsevier: Amsterdam, 2000; (e) I. Tritto, L. Boggioni and D. R. Ferro, *Coord. Chem. Rev.*, 2006, **250**, 212; (f) K. Nomura, *Chin. J. Polym. Sci.*, 2008, **26**, 513.
- 3 *Syndiotactic Polystyrene-Synthesis Characterization Processing and Applications*, J. Schellenberg, Ed.; John Wiley & Sons, Inc.: New Jersey, 2010.
- 4 (a) A. F. Mason, G. W. Coates, in *Macromolecular Engineering*, ed. K. Matyjaszewski, Y. Gnanou and L. Leibler, Wiley-VCH, Weinheim, Germany, 2007, vol. 1, p. 217; (b) *Metal Catalysts in Olefin Polymerization*, ed. Z. Guan, *Topics in Organometallic Chemistry* 26, Springer Verlag, Berlin (2009).
- 5 Reviews for metallocenes, see: (a) H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143; (b) W. Kaminsky, *Macromol. Chem. Phys.*, 1996, **197**, 3907; (c) W. Kaminsky and M. Arndt, *Adv. Polym. Sci.*, 1997, **127**, 143; (d) J. Suhm, J. Heinemann, C. Wörner, P. Müller, F. Stricker, J. Kressler, J. Okuda and R. Mülhaupt, *Macromol. Symp.*, 1998, **129**, 1.
- 6 Reviews for linked half-titanocenes, see: (a) A. L. McKnight and R. M. Waymouth, *Chem. Rev.*, 1998, **98**, 2587; (b) H. Braunschweig and F. M. Breitling, *Coord. Chem. Rev.*, 2006, **250**, 2691; (c) J. Cano and K. Kunz, *J. Organomet. Chem.*, 2007, **692**, 4411.
- 7 Reviews for nonbridged half-titanocenes, see: (a) D. W. Stephan, *Organometallics*, 2005, **24**, 2548; (b) K. Nomura, J. Liu, S. Padmanabhan and B. Kitiyanan, *J. Mol. Catal. A: Chem.*, 2007, **267**, 1; (c) K. Nomura, *Dalton Trans.*, 2009, 8811.
- 8 Reviews for post-metallocenes, see: (a) G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428; (b) V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283; (c) P. D. Bolton and P. Mountford, *Adv. Synth. Catal.*, 2005, **347**, 355; (d) K. Nomura and S. Zhang, *Chem. Rev.*, 2010, 110203132125005, DOI: 10.1021/cr100207hASAP (web released on October 29, 2010).
- 9 Selected reviews for (co)polymerisation of polar monomers, see: (a) L. S. Boffa and B. M. Novak, *Chem. Rev.*, 2000, **100**, 1479; (b) A. Nakamura, S. Ito and K. Nozaki, *Chem. Rev.*, 2009, **109**, 5215; (c) E. Y.-X. Chen, *Dalton Trans.*, 2009, 8784.
- 10 Selected reviews for living polymerisation, see: (a) G. W. Coates, P. D. Hustad and S. Reinartz, *Angew. Chem., Int. Ed.*, 2002, **41**, 2236; (b) G. J. Domski, J. M. Rose, G. W. Coates, A. D. Bolig and M. Brookhart, *Prog. Polym. Sci.*, 2007, **32**, 30; (c) L. R. Sita, *Angew. Chem., Int. Ed.*, 2009, **48**, 2464.
- 11 (a) G. W. Coates, *J. Chem. Soc., Dalton Trans.*, 2002, 467; (b) K. Nomura and B. Kitiyanan, *Curr. Org. Synth.*, 2008, **5**, 217; (c) W. Kaminsky, A. Funck and H. Hähnsen, *Dalton Trans.*, 2009, 8803.
- 12 *Frontiers in Metal-Catalysed Polymerisation* (special issue); ed. J. A. Gladysz, *Chem. Rev.* 20000, **100**(4). For example (a) S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169; (b) H. G. Alt and A. Köppl, *Chem. Rev.*, 2000, **100**, 1205; (c) E. Y.-X. Chen and T. J. Marks, *Chem. Rev.*, 2000, **100**, 1391.
- 13 *Metallocene complexes as catalysts for olefin polymerisation* (special issue); ed. H. G. Alt; *Coord. Chem. Rev.*, 2006, 250((1–2)), 1.
- 14 *Metal-catalysed Polymerisation (special issue)*; ed. B. Milani and C. Claver; *Dalton Trans.*, 2009, 8769.
- 15 (a) J. J. Schellenberg, *Prog. Polym. Sci.*, 2009, **34**, 688; (b) K. Nomura, in *Syndiotactic Polystyrene-Synthesis Characterization Processing and Applications*, ed. J. Schellenberg, John Wiley & Sons, Inc., New Jersey, 2010, p. 60; (c) K. Nomura, *Catal. Surv. Asia*, 2010, **14**, 33.
- 16 Examples for ethylene/ α -olefin copolymerisations using metallocenes and constrained geometry type catalysts, (a) K. Soga, T. Uozumi, S. Nakamura, T. Toneri, T. Teranishi, T. Sano, T. Arai and T. Shiono, *Macromol. Chem. Phys.*, 1996, **197**, 4237; (b) J. Suhm, M. J. Schneider and R. Mülhaupt, *J. Polym. Sci., Part A: Polym. Chem.*, 1997, **35**, 735; (c) J. Suhm, M. J. Schneider and R. Mülhaupt, *J. Mol. Catal. A: Chem.*, 1998, **128**, 215.
- 17 Influence of cyclopentadienyl substituents (Cp') in ethylene polymerisation by zirconocenes, P. C. Möhring and N. J. Coville, *J. Organomet. Chem.*, 1994, **479**, 1.
- 18 (a) For example, J. A. M. Canich, G. G. Hlatky, and H. W. Turner, USP 542236 (1990); (b) J. A. M. Canich, (Exxon), USP 5026798 (1991); (c) J. A. M. Canich, (Exxon), Eur. Pat. 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, and S.-Y. Lai, (Dow), Eur. Pat. Appl., 416815 (1991); (e) J. C. Stevens, and D. R. Neithamer, (Dow), Eur. Pat. Appl., 418022 (1991); (f) J. Okuda, F. J. Schattenmann, S. Wocadlo and W. Massa, *Organometallics*, 1995, **14**, 789; (g) K. L. du Plooy, U. Moll, S. Wocadlo, W. Massa and J. Okuda, *Organometallics*, 1995, **14**, 3129; (h) D. D. Devore, F. J. Timmers, D. L. Hasha, R. K. Rosen, T. J. Marks, P. A. Deck and C. L. Stern, *Organometallics*, 1995, **14**, 3132; (i) D. W. Carpenetti, L. Kloppenburg, J. T. Kupec and J. L. Petersen, *Organometallics*, 1996, **15**, 1572; (j) A. L. McKnight, M. A. Masood and R. M. Waymouth, *Organometallics*, 1997, **16**, 2879; (k) B. A. Harrington and D. J. Crowther, *J. Mol. Catal. A: Chem.*, 1998, **128**, 79; (l) A. L. McKnight and R. M. Waymouth, *Macromolecules*, 1999, **32**, 2816.
- 19 (a) P. J. Shapiro, E. Bunel, W. P. Schaefer and J. E. Bercaw, *Organometallics*, 1990, **9**, 867; (b) P. J. Shapiro, W. D. Cotter, W. P. Schaefer, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 1994, **116**, 4623.
- 20 For examples, see: (a) K. Kunz, G. Erker, S. Döring, S. Bredeau, G. Kehr and R. Fröhlich, *Organometallics*, 2002, **21**, 1031; (b) K. Kunz, G. Erker, G. Kehr, R. Fröhlich, H. Jacobsen, H. Berke and O. Blacque, *J. Am. Chem. Soc.*, 2002, **124**, 3316; (c) Syntheses and ethylene (co)polymerisation with cyclodimeric (sp²-C₁)-bridged Cp/oxido group 4 metal complexes J. Hung and R. M. Waymouth, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 3840.
- 21 Our initial efforts in olefin polymerisation and ethylene/ α -olefin copolymerisation, for example, (a) K. Nomura, N. Naga, M. Miki, K. Yanagi and A. Imai, *Organometallics*, 1998, **17**, 2152; (b) K. Nomura, N. Naga, M. Miki and K. Yanagi, *Macromolecules*, 1998, **31**, 7588; (c) K. Nomura, T. Komatsu and Y. Imanishi, *J. Mol. Catal. A: Chem.*, 2000, **152**, 249; (d) K. Nomura, K. Oya, T. Komatsu and Y. Imanishi, *Macromolecules*, 2000, **33**, 3187; (e) K. Nomura, T. Komatsu and Y. Imanishi, *J. Mol. Catal. A: Chem.*, 2000, **159**, 127; (f) K. Nomura, K. Oya and Y. Imanishi, *J. Mol. Catal. A: Chem.*, 2001, **174**, 127; (g) K. Nomura, T. Komatsu, M. Nakamura and Y. Imanishi, *J. Mol. Catal. A: Chem.*, 2000, **164**, 131.
- 22 (a) S. Zhang, W. E. Piers, X. Gao and M. Parvez, *J. Am. Chem. Soc.*, 2000, **122**, 5499; (b) S. Zhang and W. E. Piers, *Organometallics*, 2001, **20**, 2088 Synthesis of complexes and reaction chemistry with borates.
- 23 J. McMeeking, X. Gao, R. E. v. H. Spence, S. J. Brown, and D. Jeremic, USP 6114481 (2000).
- 24 (a) K. Nomura, K. Fujita and M. Fujiki, *Catal. Commun.*, 2004, **5**, 413; (b) K. Nomura, K. Fujita and M. Fujiki, *J. Mol. Catal. A: Chem.*, 2004, **220**, 133.
- 25 (a) A. R. Dias, M. T. Duarte, A. C. Fernandes, S. Fernandes, M. M. Marques, A. M. Martins, J. F. da Silva and S. S. Rodrigues, *J. Organomet. Chem.*, 2004, **689**, 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 and C. Wilson, *J. Organomet. Chem.*, 2005, **690**, 874; (c) M. J. Ferreira and A. M. Martins, *Coord. Chem. Rev.*, 2006, **250**, 118.

- 26 (a) D. W. Stephan, J. C. Stewart, F. Guérin, R. E. v. H. Spence, W. Xu and D. G. Harrison, *Organometallics*, 1999, **18**, 1116; (b) D. W. Stephan, J. C. Stewart, S. J. Brown, J. W. Swabey, and Q. Wang, EP881233 A1 (1998); (c) 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 and D. G. Harrison, *Organometallics*, 2003, **22**, 1937.
- 27 W. P. Kretschmer, C. Dijkhuis, A. Meetsma, B. Hessen and J. H. Teuben, *Chem. Commun.*, 2002, 608.
- 28 Ethylene copolymerisation with 2-methyl-1-pentene (disubstituted α -olefin), (a) K. Nomura, K. Itagaki and M. Fujiki, *Macromolecules*, 2005, **38**, 2053; (b) K. Itagaki, M. Fujiki and K. Nomura, *Macromolecules*, 2007, **40**, 6489.
- 29 Copolymerisation with α -olefin containing bulky substituents, (a) K. Nomura and K. Itagaki, *Macromolecules*, 2005, **38**, 8121; (b) F. Z. Khan, K. Kakinuki and K. Nomura, *Macromolecules*, 2009, **42**, 3767; (c) K. Kakinuki, M. Fujiki and K. Nomura, *Macromolecules*, 2009, **42**, 4585.
- 30 Copolymerisation with norbornene, (a) K. Nomura, M. Tsubota and M. Fujiki, *Macromolecules*, 2003, **36**, 3797; (b) W. Wang, T. Tanaka, M. Tsubota, M. Fujiki, S. Yamanaka and K. Nomura, *Adv. Synth. Catal.*, 2005, **347**, 433; (c) K. Nomura, W. Wang, M. Fujiki and J. Liu, *Chem. Commun.*, 2006, 2659; (d) K. Nomura, J. Yamada, W. Wang and J. Liu, *J. Organomet. Chem.*, 2007, **692**, 4675.
- 31 Copolymerisation with cyclohexene, cyclopentene, (a) W. Wang, M. Fujiki and K. Nomura, *J. Am. Chem. Soc.*, 2005, **127**, 4582; (b) J. Liu and K. Nomura, *Adv. Synth. Catal.*, 2007, **349**, 22352007.
- 32 Copolymerisation with styrene with efficient styrene incorporation or in a living manner, (a) K. Nomura, T. Komatsu and Y. Imanishi, *Macromolecules*, 2000, **33**, 8122; (b) K. Nomura, H. Okumura, T. Komatsu and N. Naga, *Macromolecules*, 2002, **35**, 5388; (c) H. Zhang and K. Nomura, *J. Am. Chem. Soc.*, 2005, **127**, 9364; (d) H. Zhang and K. Nomura, *Macromolecules*, 2006, **39**, 5266; (e) H. Zhang, D.-J. Byun and K. Nomura, *Dalton Trans.*, 2007, 1802; (f) K. Nomura, H. Zhang and D.-J. Byun, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 4162.
- 33 First patent application for Cp'-aryloxo complexes, K. Nomura, N. Naga, JPKokai H11-166010 (June 22, 1999), applied on January 29, 1997 (Japanese Patent 3934768, 2007).
- 34 Related publications for synthesis and reactivity of cationic half-titanocene alkyl complexes containing aryloxo ligand, (a) J. S. Vilardo, M. G. Thorn, P. E. Fanwick and I. P. Rothwell, *Chem. Commun.*, 1998, 2425; (b) M. G. Thorn, J. S. Vilardo, P. E. Fanwick and I. P. Rothwell, *Chem. Commun.*, 1998, 2427; (c) M. G. Thorn, J. S. Vilardo, J. Lee, B. Hanna, P. E. Fanwick and I. P. Rothwell, *Organometallics*, 2000, **19**, 5636.
- 35 Related study (by the other group) concerning structure and activity correlation, effect of ion pairing and sterics on chain propagation for olefin polymerisation by half-titanocenes containing aryloxides, see: (a) T. A. Manz, K. Phomphrai, G. Medvedev, B. B. Krishnamurthy, S. Sharma, J. Haq, K. A. Novstrup, K. T. Thomson, W. N. Delgass, J. M. Caruthers and M. M. Abu-Omar, *J. Am. Chem. Soc.*, 2007, **129**, 3776; (b) T. A. Manz, S. Sharma, K. Phomphrai, K. A. Novstrup, A. E. Fenwick, P. E. Fanwick, G. A. Medvedev, M. M. Abu-Omar, W. N. Delgass, K. T. Thomson and J. M. Caruthers, *Organometallics*, 2008, **27**, 5504; (c) More recent examples for catalyst development (improvement?) in ethylene/ α -olefin copolymerisation using Cp*-aryloxo analogues on the basis of our previous reports, concepts for the catalyst design,^{7b,c,21a}T.-J. Kim, S.-K. Kim, B.-J. Kim, J. S. Hahn, M.-A. Ok, J. H. Song, D.-H. Shin, J. Ko, M. Cheong, J. Kim, H. Won, M. Mitoraj, M. Srebro, A. Michalak and S. O. Kang, *Macromolecules*, 2009, **42**, 6932.
- 36 C. Beddie, E. Hollink, P. Wei, J. Gauld and D. W. Stephan, *Organometallics*, 2004, **23**, 5240.
- 37 (a) E. G. Ijpeij, M. A. Zuideveld, H. J. Arts, F. van der Burgt and G. H. J. van Doremaele, WO, 2007031295, 2007; (b) E. G. Ijpeij, P. J. H. Windmuller, H. J. Arts, F. van der Burgt, G. H. J. van Doremaele and M. A. Zuideveld, WO, 2005090418, 2005. Recent patent application for Cp'TiX₂{N=C(Ar)NR₂} (X = Cl, Me; Ar = 2,6-F₂C₆H₃; R = 'Pr).
- 38 H. Ishino, S. Takemoto, K. Hirata, Y. Kanaizuka, M. Hidai, M. Nabika, Y. Seki, T. Miyatake and N. Suzuki, *Organometallics*, 2004, **23**, 4544.
- 39 I. Saeed, S. Katao and K. Nomura, *Organometallics*, 2009, **28**, 111.
- 40 I. Saeed, S. Katao and K. Nomura, *Inorg. Chem.*, 2009, **48**, 5011.
- 41 (a) N. Tomotsu, N. Ishihara, T. H. Newman and M. T. Malanga, *J. Mol. Catal. A: Chem.*, 1998, **128**, 167; (b) N. Tomotsu and N. Ishihara, *Catal. Surv. Jpn.*, 1997, **1**, 89.
- 42 K. Itagaki, S. Hasumi, M. Fujiki and K. Nomura, *J. Mol. Catal. A: Chem.*, 2009, **303**, 102.
- 43 Syntheses of half-zirconocenes containing aryloxo ligands and their use as the catalyst precursors for ethylene polymerisation, 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 and J. V. Santos, *Organometallics*, 2000, **19**, 2837.
- 44 K. Nomura, A. Tanaka and S. Katao, *J. Mol. Catal. A*, 2004, **254**, 197.
- 45 P. Gomez-Sal, A. Martin, M. Mena, P. Royo and R. Serrano, *J. Organomet. Chem.*, 1991, **419**, 77.
- 46 S. J. Sturla and S. L. Buchwald, *Organometallics*, 2002, **21**, 739.
- 47 K. Nomura and A. Fudo, *Inorg. Chim. Acta*, 2003, **345**, 377. The reaction of Cp*TiMe₂(O-2,6-Pr₂C₆H₃) with B(C₆F₅)₃ in toluene-*d*₈ cleanly gave Cp*Ti(C₆F₅)[CH₂B(C₆F₅)₂](O-2,6-Pr₂C₆H₃) upon stirring for long hours, unpublished results.
- 48 K. Nomura, unpublished results (but presented on many occasions in the symposium, lectures).
- 49 K. Nomura and A. Fudo, *J. Mol. Catal. A: Chem.*, 2004, **209**, 9.
- 50 (a) S. Anfang, K. Harms, F. Weller, O. Borgmeier, H. Lueken, H. Schilder and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1998, **624**, 159; (b) T. Rubenstahl, F. Weller, S. Wacaldo, W. Massa and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1995, **621**, 953.
- 51 (a) N. Yue, E. Hollink, F. Guérin and D. W. Stephan, *Organometallics*, 2001, **20**, 4424; (b) E. Hollink, P. Wei and D. W. Stephan, *Organometallics*, 2004, **23**, 1562.
- 52 C. Beddie, E. Hollink, P. Wei, J. Gauld and D. W. Stephan, *Organometallics*, 2004, **23**, 5240.
- 53 K. Nomura, H. Fukuda, S. Katao, M. Fujiki, H.-Y. Kim, D.-H. Kim and I. Saeed, *Macromolecules*, 2011, in press (web released on March 4).
- 54 For selected examples (MAO co-catalyst), see: (a) N. Ishihara, T. Seimiya, M. Kuramoto and M. Uoi, *Polym. Prepr. Jpn.*, 1986, **35**, 240; (b) N. Ishihara, T. Seimiya, M. Kuramoto and M. Uoi, *Macromolecules*, 1986, **19**, 2464; (c) A. Zambelli, P. Longo, C. Pellecchia and A. Grassi, *Macromolecules*, 1987, **20**, 2035; (d) N. Ishihara, T. Seimiya, M. Kuramoto and M. Uoi, *Macromolecules*, 1988, **21**, 3356; (e) A. Zambelli, L. Oliva and C. Pellecchia, *Macromolecules*, 1989, **22**, 2129; (f) W. Kaminsky, S. Lenk, V. Scholz, H. W. Roesky and A. Herzog, *Macromolecules*, 1997, **30**, 7647; (g) N. Tomotsu, H. Shouzaki, M. Aida, M. Takeuchi, K. Yokota, Y. Aoyama, S. Ikeuchi, and T. Inoue, ed. M. Terano and T. Shiono, In: *Future Technology for Polyolefin and Olefin Polymerisation Catalysis*, Technology and Education Publishers, Tokyo, 2002, pp 49–54.
- 55 Example concerning syndiospecific styrene polymerisation by half-titanocene complex-borate catalyst, (a) A. Grassi, C. Lamberti, A. Zambelli and I. Mingozzi, *Macromolecules*, 1997, **30**, 1884; (b) A. Grassi, S. Saccheo, A. Zambelli and F. Laschi, *Macromolecules*, 1998, **31**, 5588; (c) N. Tomotsu, H. Shouzaki and M. Takeuchi, *Polym. Prepr. Jpn.*, 1998, **47**, 1597.
- 56 (a) K. Soga, D. H. Lee and H. Yanagihara, *Polym. Bull.*, 1988, **20**, 237; (b) P. Mani and C. M. Burns, *Macromolecules*, 1991, **24**, 5476; (c) Ed. D. B. Priddy, Y. W. Cheung, M. J. Guest and J. Scheirs, In: *Modern Styrenic Polymers: Polystyrenes and Styrenic Copolymers*, John Wiley & Sons Ltd., 2003, 605.
- 57 For example, (a) H. Chen, M. J. Guest, S. Chum, A. Hiltner and E. Baer, *J. Appl. Polym. Sci.*, 1998, **70**, 109; (b) P. S. Chum, W. J. Kruper and M. J. Guest, *Adv. Mater.*, 2000, **12**, 1759; (c) Y. W. Cheung and M. J. Guest, *J. Polym. Sci., Part B: Polym. Phys.*, 2000, **38**, 2976.
- 58 Examples in ethylene/styrene copolymerisation, (a) P. Longo, A. Grassi and L. Oliva, *Makromol. Chem.*, 1990, **191**, 2387; (b) C. Pellecchia, D. Pappalardo, M. D'Arco and A. Zambelli, *Macromolecules*, 1996, **29**, 1158; (c) L. Oliva, S. Mazza and P. Longo, *Macromol. Chem. Phys.*, 1996, **197**, 3115; (d) G. Xu and S. Lin, *Macromolecules*, 1997, **30**, 685; (e) D. H. Lee, K. B. Yoon, H. J. Kim, S. S. Woo and S. K. Noh, *J. Appl. Polym. Sci.*, 1998, **67**, 2187.
- 59 (a) J. C. Stevens, F. J. Timmers, D. R. Wilson, G. F. Schmidt, P. N. Nickias, R. K. Rosen, and G. W. Knight, S. Y. Lai, EP 0416815 A2, 1991; (b) F. J. Timmers, USP 6670432 B1, 2003; (c) D. J. Arriola, M. Bokota, R. E. Campbell Jr., J. Klosin, R. E. LaPointe, O. D. Redwine, R. B. Shankar, F. J. Timmers and K. A. Abboud, *J. Am. Chem. Soc.*, 2007, **129**, 7065.

- 60 (a) F. G. Sernetz, R. Mülhaupt and R. M. Waymouth, *Macromol. Chem. Phys.*, 1996, **197**, 1071; (b) F. G. Sernetz, R. Mülhaupt, F. Amor, T. Eberle and J. Okuda, *J. Polym. Sci., Part A: Polym. Chem.*, 1997, **35**, 1571; (c) T. A. Sukhova, A. N. Panin, O. N. Babkina and N. M. Bravaya, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 1083.
- 61 (a) G. Xu, *Macromolecules*, 1998, **31**, 2395; (b) M. Kamigaito, T. K. Lal and R. M. Waymouth, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 4649; (c) K. Nomura, H. Okumura, T. Komatsu, N. Naga and Y. Imanishi, *J. Mol. Catal. A: Chem.*, 2002, **190**, 225.
- 62 (a) N. Guo, L. Li and T. J. Marks, *J. Am. Chem. Soc.*, 2004, **126**, 6542; (b) H. Li and T. J. Marks, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15295; (c) N. Guo, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 2008, **130**, 2246.
- 63 L. Oliva, L. Caporaso, C. Pellecchia and A. Zambelli, *Macromolecules*, 1995, **28**, 4665.
- 64 (a) L. Caporaso, L. Izzo and L. Oliva, *Macromolecules*, 1999, **32**, 7329; (b) L. Caporaso, L. Izzo, S. Zappile and L. Oliva, *Macromolecules*, 2000, **33**, 7275.
- 65 (a) T. Arai, T. Ohtsu and S. Suzuki, *Macromol. Rapid Commun.*, 1998, **19**, 327; (b) T. Arai, S. Suzuki, and T. Ohtsu, In: *Olefin Polymerisation: Emerging Frontiers*, ed. P. Arjunan, ACS Symposium Series 749, American Chemical Society, Washington, D. C., 2000, 66; (c) T. Arai, T. Ohtsu and M. Nakajima, *Polym. Prepr. Jpn.*, 1999, **48**, 1666.
- 66 L. Izzo, M. Napoli and L. Oliva, *Macromolecules*, 2003, **36**, 9340.
- 67 Examples of a mechanistic studies for styrene polymerisation, (a) A. Grassi, A. Zambelli and F. Laschi, *Organometallics*, 1996, **15**, 480; (b) G. Minieri, P. Corradini, G. Guerra, A. Zambelli and L. Cavallo, *Macromolecules*, 2001, **34**, 5379; (c) M. K. Mahanthappa and R. M. Waymouth, *J. Am. Chem. Soc.*, 2001, **123**, 12093.
- 68 D.-J. Byun, A. Fudo, A. Tanaka, M. Fujiki and K. Nomura, *Macromolecules*, 2004, **37**, 5520.
- 69 K. Nomura and K. Fujii, *Macromolecules*, 2003, **36**, 2633.
- 70 H. Zhang, S. Katao, K. Nomura and J. Huang, *Organometallics*, 2007, **26**, 5967.
- 71 (a) C. Pellecchia, M. Mazzeo and G.-J. Gruer, *Macromol. Rapid Commun.*, 1999, **20**, 337; (b) C. Pellecchia, D. Pappalardo, L. Oliva, M. Mazzeo and G.-J. Gruer, *Macromolecules*, 2000, **33**, 2807.
- 72 According to the described experimental procedures (including the results regarding T_g values of the resultant polymers),^{26b} it is not yet clear whether or not the styrene contents reported here may include atactic/syndiotactic polystyrene. The M_w/M_n values in certain polymerisation runs also were somewhat broad.
- 73 However, this switch by the Cp'-aryloxy analogues were dependent upon the cyclopentadienyl fragment (Cp'), the polymerisation temperature, styrene/ethylene molar ratio, and SPS was accompanied under certain conditions.^{32f} The fact would also support the proposed equilibrium shown in Scheme 12.^{32f}