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Feature Article

Polymerization with Dinuclear Metallocene Compounds

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Abstract : The metallocene compounds had been applied to the polymerizations of olefins and vinyl monomers with methylaluminoxane (MAO) cocatalyst, and they have usually one transition metal atom per molecule, i.e., mononuclear metallocene. Recently it has been found that the dinuclear metallocene compounds containing two transition metal atoms exhibit the peculiar polymerization behaviors for olefins and vinyl monomers. In this article, the dinuclear metallocenes are classified into four groups of dinuclear bent-metallocene, dinuclear ansa-metallocene, dinuclear constrained geometry catalyst and dinuclear half-metallocene, and then the synthesis of dinuclear metallocene of each group as well as the polymerization behaviors for ethylene, propylene, and styrene are described.

Introduction

The group 4 metallocene complexes are of increasing interest in relation to many catalytic reactions, particularly in homogeneous olefin polymerization.¹⁻⁴ As an advantage over the conventional Ziegler-Natta system, the metallocene catalyst system combines high activity with the

possibility of tailoring the polymer properties such as molecular weight, molecular weight distribution as well as stereochemistry through an appropriate ligand design at the metal center.

Recently a variety of dinuclear metallocene compounds, which contain two mechanically linked metallocene units, have been prepared to examine their catalytic properties. Dinuclear metallocene have been paid attentions in two respects. First, dinuclear metallocenes can be a new kind of met-

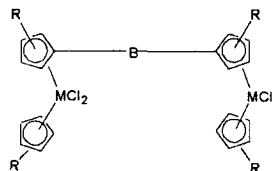
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allocene catalyst for olefin polymerization which could be potentially useful in catalyst for olefin if two metal centers show cooperative electronic and steric effects on catalytic reaction. Second, dinuclear metallocenes could be good model to probe reaction characterization of an immobilized metallocene because the immobilized metallocene could be regarded as a multinuclear metallocene. In 1989, Patterson prepared a series of dinuclear zirconocene complexes $[X(C_5H_4)_2][(C_5R_5)ZrCl_2]_2$ ($X=CH_2, SiMe_2, R=H, CH_3$), which contain two connected zirconocene dichloride unit and examined the structural response of the $[SiMe_2(C_5H_4)_2]^{-2}$ ligand to changes in the metal coordination environment.⁵ Recently, Royo described the synthesis, reactivities and characterization of dinuclear metallocene complexes of titanium and zirconium with $[SiMe_2(C_5H_5)_2]^{-2}$ as a bridge ligand, and directly linked two Cp's extensively.⁶⁻¹¹ Although these very interesting dinuclear metallocene complexes are well represented, relatively few publications have illustrated the utilization of dinuclear metallocene as an olefin polymerization catalyst.

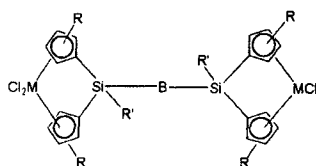
In 1993, Mülhaupt reported olefin polymerization behaviors of the dinuclear zirconocene for the first time.¹² He successfully prepared the phenylene bridged dinuclear zirconocenes and demonstrated differences of polymerization properties between the dinuclear compound and the corresponding mononuclear compound. Subsequently Green,^{13,14} Corey,¹⁵⁻¹⁷ Aulbach,¹⁸ Spaleck,¹⁹ and Soga²⁰ synthesized a variety group of dinuclear metallocene of titanium and zirconium to investigate catalytic properties and analyzed the results. Actually the first systematic polymerization study about the dinuclear metallocene in terms of the structural characteristics of the bridge ligand have been performed by us.²¹⁻³³ According to our studies it is clear that the dinuclear metallocenes display not only the distinguished properties from the known well-defined mononuclear metallocenes, but also a strong dependence upon the length as well as the type of the bridge ligand.

Here we review the development of dinuclear metallocene as polymerization catalyst. This review focuses on the polymerization behaviors of dinuclear metallocenes with the emphasis on the role of the bridging ligand in the polymerization cata-

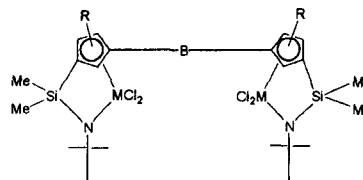
Class I : Dinuclear Bent-Metallocene



Class II : Dinuclear Ansa-Metallocene



Class III : Dinuclear Constrained Geometry Catalyst



Class IV : Dinuclear Half-Metallocene

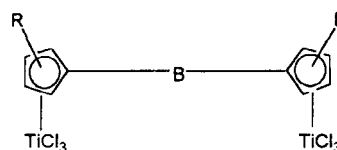


Figure 1. Classification of dinuclear metallocenes.

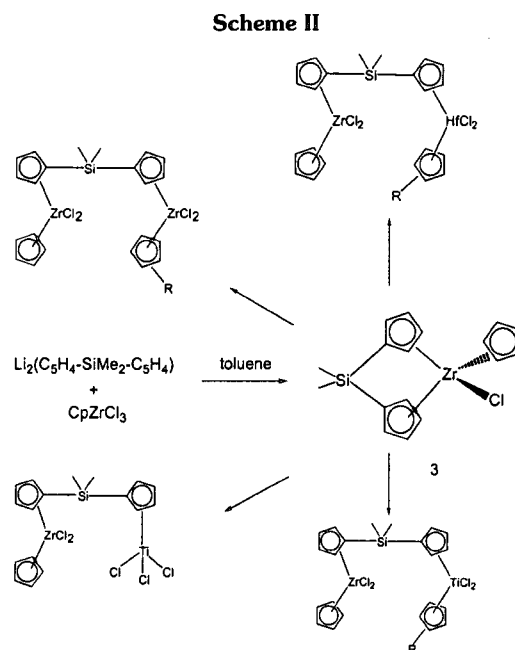
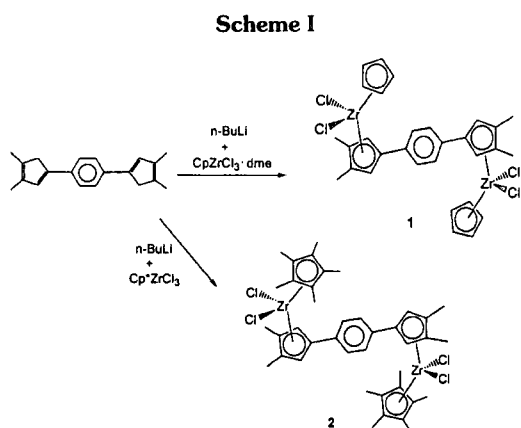
lysts. For the convenience, the dinuclear metallocenes are classified into four groups on the basis of the structure as shown in Figure 1.

This review does not cover the several closely related areas of dinuclear metallocenes such as Pattersons structural studies of $[X(C_5H_4)_2][(C_5R_5)ZrCl_2]_2$ ($X=CH_2, SiMe_2$),⁵ Royo's extensive studies of dinuclear half-metallocenes, bent-metallocenes and late-late bimetallic metallocenes,⁶⁻¹¹ and Corey's studies of catalytic decoupling of $PhSiH_3$ using dinuclear metallocenes¹⁵⁻¹⁷ and double-bridged dinuclear metallocenes,³⁴⁻³⁶ including heterometallic dinuclear metallocenes,³⁷ early-late bimetallic metallocenes,^{38,39} and cationic dinuclear species.⁴⁰

Dinuclear Bent-Metallocene

The most studied dinuclear bent-metallocene is the dinuclear metallocene that two bent-metal-

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locene units, $Cp^*_2MCl_2$, are attached through the bridge ligand as shown in Figure 1.

The first dinuclear bent-metallocene employed in olefin polymerization was reported in 1993 by Mülhaupt.¹² He synthesized phenylene bridged dinuclear zirconocenes **1** and **2** as shown in Scheme I, and introduced to the propylene polymerization.

It was found that the molecular weight of polypropylenes from the dinuclear catalyst was smaller than that of the polypropylene from the corresponding mononuclear one as a result of the cooperative electron-withdrawing effect interacting two zirconium centers via the bridge. Probably the most important feature in his observation is that the cooperative interaction is working upon the dinuclear metallocene.

In 1996, Green prepared a series of dimethylsilyl-bridged dinuclear metallocenes of the group IV transition metals as shown in Scheme II and carried out olefin polymerization with them.¹⁴

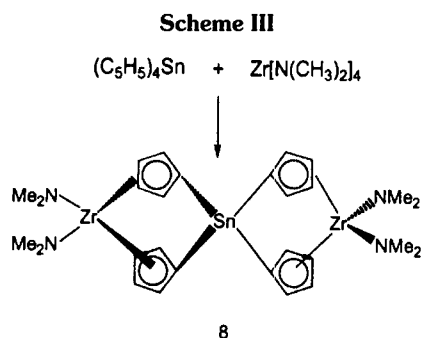
The prepared dinuclear complexes along with the corresponding mononuclear complex were tested with MAO in olefin polymerization. The results exhibited some interesting points and a part of the results are summarized in Table I.

In terms of activity, the mononuclear Kaminsky catalyst **4** displays high activity than the dimethylsilyl-bridged catalyst **5** but lower activity than both the indenyl substituted dinuclear catalyst **6** and the $(Me_2SiCH_2CH_2SiMe_2)$ -bridged dinuclear catalyst **7**. On the other hand, molecular weights of the polyethylenes from all dinuclear zirconocenes are larger than that of the polyethylene from **4**.

These results clearly support that the character-

Table I. Result of Ethylene Polymerization Catalyzed with Green's Dinuclear Complexes

	4	5	6	7
Activity (g PE/mol · M · h)	3.6×10^6	2.9×10^5	8.7×10^6	$< 1.0 \times 10^6$
$M_n \times (10^{-4})$	9.9	13.1	17.0	-
M_w/M_n	2.5	5.4	2.5	-



istics of the dinuclear metallocenes can be directed and adjusted by the nature of bridge structure as well as the ligand bonded with metal.

One very interesting spiro cyclic dinuclear metallocene came out in 1996 by W.A.Hermann.⁴¹ He reported the synthesis of tin-bridged dinuclear zirconocene as shown in Scheme III and its polymerization result.

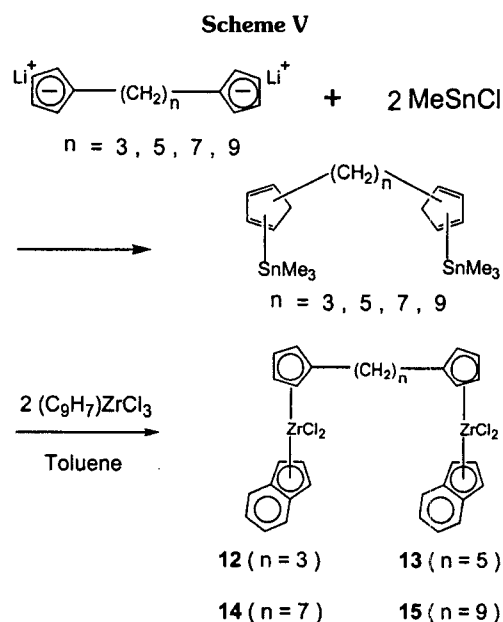
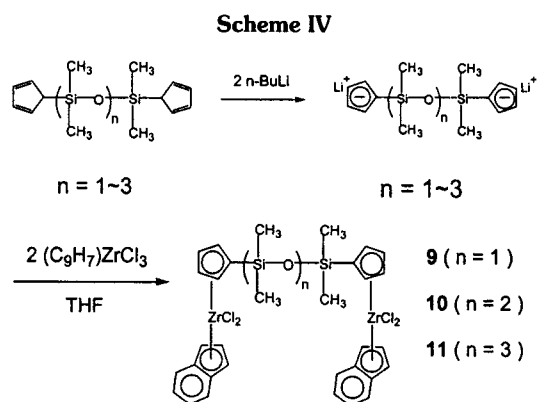
The tin-bridged dinuclear complex exhibits only 50% of the activity of the mononuclear tin-bridged ansa-metallocene while the molecular weight produced by the dinuclear complex is much higher. It was proposed that only one center of the dinuclear catalyst is active during polymerization. The activities of the Sn- and Si- bridged mononuclear complexes are comparable.

The systematic polymerization studies of the dinuclear have been performed by us with the polysiloxane- and polymethylene-bridged dinuclear metallocenes.^{22, 23, 25, 26, 29} Over the last several years we have not only accomplished the synthesis and characterization of various new types of dinuclear metallocenes, but also probed the polymerization behaviors of these compounds.

The polysiloxane-bridged dinuclear zirconocenes were prepared as shown in Scheme IV, and the preparation of polymethylene-bridged ones has been achieved via the distannylated compounds as shown in Scheme V.

These dinuclear complexes **9~15** along with the mononuclear complex **16**, CpIndZrCl₂, were tested with MMAO as a cocatalyst in the polymerization of ethylene and the results are shown in Table II.

In our investigations, the polymerization activity among the catalysts decreased in the order **16** > **11** > **10** > **9**, which indicated the dinuclear zircono-



cene with polysiloxane-bridged ligand represented smaller activity than the mononuclear zirconocene. On the other hand, the activities of the polymethylene-bridged dinuclear zirconocenes exhibited greater activity than that of the mononuclear zirconocene as well as those of the polysiloxane-bridged dinuclear metallocenes.

From a stand point of the catalyst activity, there are some important points to be noted to characterize the dinuclear metallocene complexes. The prime feature is that the activity increases as the bridge ligand becomes longer. The relation between the number of atoms in the bridge ligand and activities of the dinuclear metallocenes is dis-

Table II. Result of Ethylene Polymerization Catalyzed with Dinuclear Zirconocenes 9~15 and Mononuclear Complex 16

Catalyst	Activity	$M_w (\times 10^{-3})$	M_w/M_n	T_m (°C)
9	1,762	450	4.8	135
10	2,187	442	4.6	134
11	2,451	350	3.4	135
12	2,573	-	-	134
13	3,884	390	3.4	135
14	4,602	-	-	135
15	5,550	-	-	135
16	2,647	163	2.7	134

Activity (kg PE/mol Zr · h · atm).

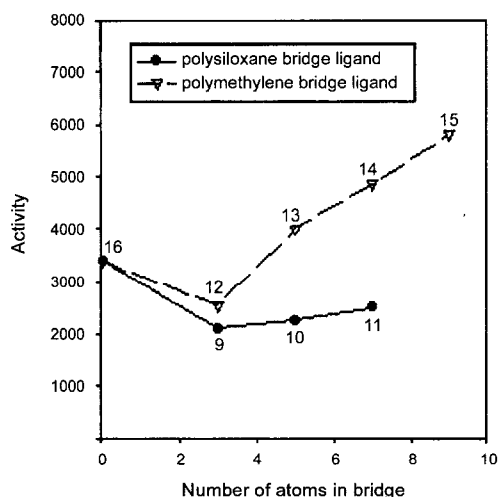


Figure 2. Variation of activity (kg PE/mol Zr · h · atm) with number of atoms in bridge ligand.

played in Figure 2.

It is remarkable that the activity increases steeply and steadily with the number of atoms in the bridge ligand. The second feature is the effect of the bridge ligand structure. The addition of one methylene unit in the bridge exerts 500 kg of PE/mol of Zr · h · atm on activity while one siloxane unit in the bridge corresponds to 340 kg of PE/mol of Zr · h · atm. In terms of bridge ligand effect, the polymethylene bridges give more impact on both the activity values and the increasing rate of activity of the dinuclear zirconocenes.

As shown in Figure 3, it is consistently observed that molecular weights of polyethylenes generated by the dinuclear zirconocenes are much greater than that of polyethylene by the mononuclear zir-

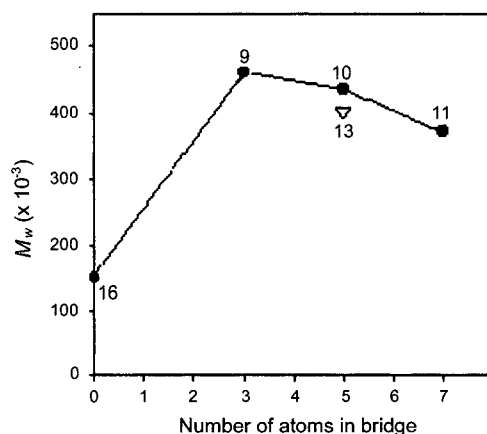


Figure 3. Molecular weights of polyethylenes produced from dinuclear zirconocenes with number of atoms in bridge ligand.

conocene. The relatively shorter bridged dinuclear complex generates a higher molecular weight polymer among the dinuclear catalysts. The molecular weight distributions of polyethylenes from the dinuclear complexes ranged from 3.4 to 4.8, which are fairly broadened values when compared to that of polymer produced by the mononuclear metallocene catalyst.

In other works related to polymerization behavior of dinuclear metallocenes, a structure-performance relation has not discussed extensively. We thus would like to relate electronic and steric influences to catalytic activity and molecular weight of polyethylene to understand the trend noted in experiments.^{26,29} It is generally accepted that the activity and molecular weight increase with increasing electron density at the active center. In polymeri-

zation experiments, the polymerization activity of catalysts decreased in the order **15**>**14**>**13**>**16**>**12**>**11**>**10**>**9**, which indicated the dinuclear zirconocenes with polymethylene bridges with more than 5 methylenic unit showed greater activity than the mononuclear one. On the other hand, the dinuclear zirconocene with polysiloxane bridge and trimethylene bridge exhibited smaller activity than the mononuclear one. These outcomes can be explained by electronic and steric influences of the dinuclear zirconocenes.

It is understandable that the more electron density delivered by the existence of longer polymethylene bridge could stabilize the active site to accelerate the rate of polymerization as well as to improve molecular weight of polyethylene. In case of polysiloxane bridges, the Lewis acid-base interaction can be considered to explain the significant reduction in activity and molecular weight of polyethylene. It is not so surprising to think about the interaction of the Lewis acidic aluminum cocatalyst with the Lewis base oxygen at polysiloxane moiety. This operation must be an electron-withdrawing one in nature that would not only decrease the activity but also shorten the polymer length concerning the effect of steric congestion around metal center on activity.

It is known that steric hindrance prevents facile access to the coordination site to slow down the propagation rate. On this basis, it is acceptable to anticipate that the dinuclear metallocene with shorter bridge ligand experiences more steric disturbance than the one with a longer bridge ligand. As can be seen from the polymerization data, this anticipation is well in accord with the observed results. As for the steric effect on chain termination in olefin polymerization, it has been proposed that the presence of a larger substituent at the Cp ring suppress β -H transfer to the zirconium and thus makes chain termination difficult. The molecular weights of the polymer obtained with the dinuclear zirconocenes are reasonably well correlated with the proposal. The dinuclear zirconocenes with short bridge ligand should impose enhanced rigidity to the active site resulting in the formation of longer polyethylene chains, and the mononuclear zirconocene without this rigidity produces the shorter polyethylene chains. Although there

are some difficulties in rationalizing all the results, the steric influence is likely to be more pronounced than the electronic effect in directing polymerization of the dinuclear zirconocenes.

Dinuclear Ansa-Metallocene

The dinuclear metallocene containing two ansa-metallocenes was reported by Aulbach,¹⁸ Spaleck¹⁹ and Soga.²⁰ Contrary to the dinuclear bent-metallocenes bonded through the two Cp derivatives, two ansa-metallocenes reported are connected through two Si atoms.

Spaleck reported dinuclear ansa-zirconocenes,¹⁹ and he intended to bring two active species into close vicinity by a structural bridge to investigate reactions between two active centers, either contributing to deactivation or influencing polymerization by exchange of polymer chains from one active center to another one. Two dinuclear ansa-zirconocenes were synthesized as shown in Scheme VI.

The dinuclear complex results in an isomer mix-

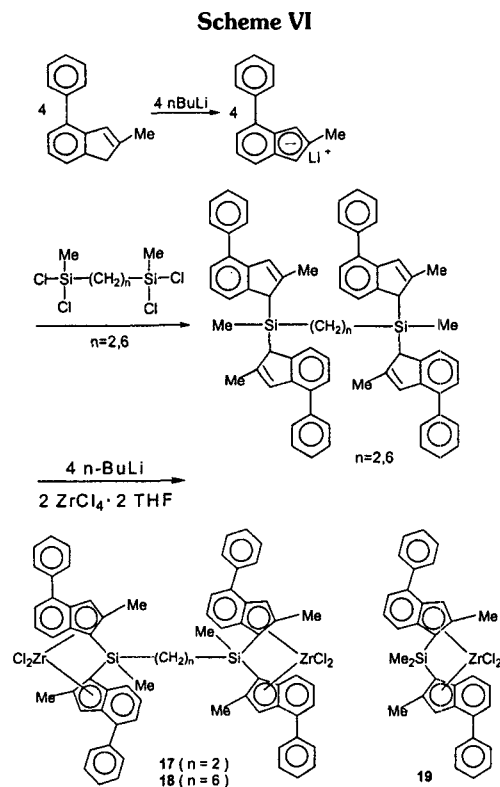


Table III. Polymerization of Liquid Propylene with Catalyst 17, 18 and 19

Catalyst	Activity	$M_w (\times 10^{-3})$	M_w/M_n	aPP(wt%)	T_m (°C)
17	50	620	4.7	6.1	153
18	93	780	2.7	2.4	154
19	765	740	2.7	< 0.2	159

Polymerization conditions : $T_p = 70^\circ\text{C}$, $[\text{Al}]/[\text{Zr}] = 12,000$.

Activity : kg PP/mmol · Zr · h.

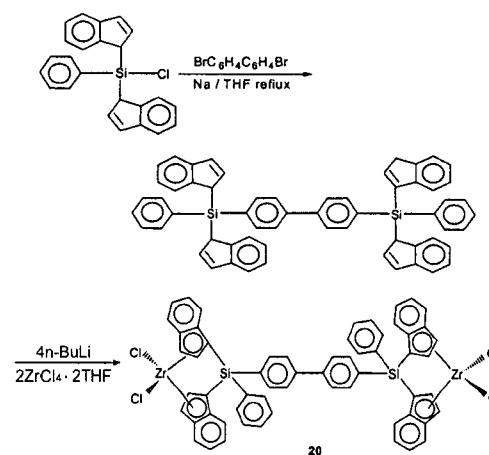
ture. This mixture should contain three different isomers: rac-rac, rac-meso and meso-meso, in which rac and meso are the chiral racemic complex **19** and its achiral meso stereoisomer. In both cases of **17** and **18**, the mixture could not be resolved.

The prepared dinuclear metallocenes **17** and **18** were tested with MAO as a cocatalyst in polymerizations of liquid polypropylene at 70°C (Table III).

The activities of dinuclear ansa-zirconocenes **17** and **18** are only in the range of 10% of the activity of mononuclear complex **19**, while the molecular weights are roughly the same as with **19** and melting points of polymer are reduced by $5\text{--}6^\circ\text{C}$. For the first time, an extremely lower activity by the dinuclear metallocene comparing with the mononuclear metallocene was observed. Considering other works done so far, this result is very unusual and there is no way to explain on the basis of an electronic or a steric reason caused by the active site. As the active site structure is encountered with the same ligand surrounding in both **17/18** and **19**, the chain termination rate should stay the same. Thus authors attributed the reason of lower activity to the lower number of active sites and several influence factors can be discussed:

- 50% or even more of the zirconium centers are within meso-indenyl moieties and practically do not contribute to productivity,
- poor solubility of the dinuclear species in liquid propylene due to their high molecular weight,
- enhanced rate of bimolecular deactivation.

According to the experimental results, the dimerization of mononuclear catalyst **19** to the dinuclear species **17** and **18** is expected to reduce regioselectivity of the polymerization centers. Within **17** and **18** the slight distortions of complex geometry to promote regioirregular insertion,

Scheme VII


compared with **19**, might be due to substitution of methyl groups on the bridge methylene groups or steric interference of the two neighbored complex moieties.

Soga prepared a novel dinuclear ansa-zirconocene complex **20** by a Wurtz coupling reaction as shown in Scheme VII.²⁰

The main objective of his study was to prepare a metallocene catalyst with a high thermal stability. The complex **20** holding $\text{C}_6\text{H}_5[\text{Si}(\text{C}_6\text{H}_5)]_2\text{C}_6\text{H}_5$ backbone looks extremely rigid, suggesting that its stability at elevated temperature might be much higher than others. Ethylene polymerization was conducted with complex **20** and the corresponding mononuclear ansa-zirconocene $[\text{Ph}_2\text{Si}(\text{Ind})_2] \text{ZrCl}_2$, **21**, for reference. It is apparent that the dinuclear complex **20** represents greater activity as compared to the mononuclear catalyst **21**. In addition, the polymerization activity increased monotonously from 40 up to 100°C . This result could be interpreted by the cooperating interaction between the adjacent zirconocenes which are electronically coupled via a biphenyl bridge. On

the other hand, the weight-average molecular weight of polyethylene decreased substantially with an increase in the polymerization temperature. The dinuclear ansa-zirconocene yielded polyethylene with a broader molecular mass distribution, which may reflect the difference in catalytic performance between two diastereomers.

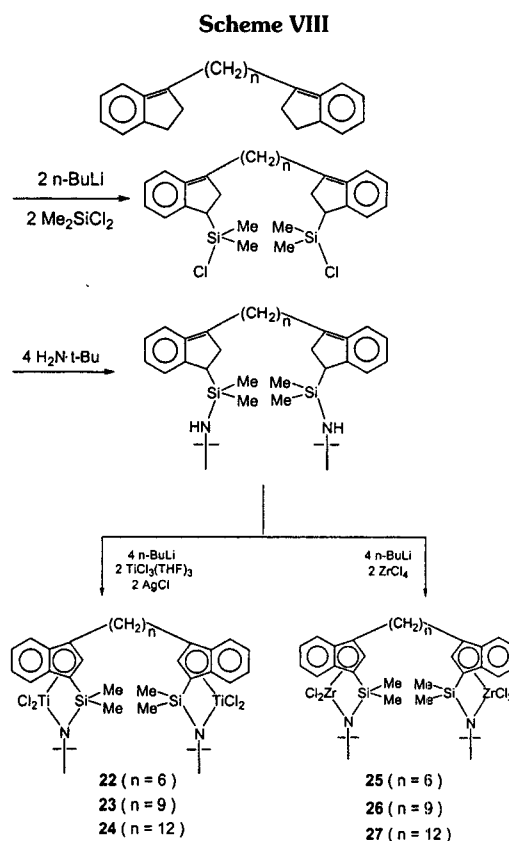
In summary, it turns out that the dinuclear ansa-zirconocene with $C_6H_5[Si(C_6H_5)]_2C_6H_5$ bridge exhibits very high activity in ethylene polymerization. On the other hand, the dinuclear ansa-zirconocenes with $-Si(Me)-(CH_2)_n-(Me)Si-$ bridges showed extremely poor polymerization activity in propylene polymerization as well as lower stereoregularity. At the moment, it is not clear to understand these results precisely. A systematic approach has to be done to characterize the properties of the dinuclear ansa-metalocene and to understand the role of the bridging ligand nature with a group of catalyst designed to direct this target.

Dinuclear Constrained Geometry Catalyst

The constrained geometry catalyst (CGC) having the formula $R_2Si(C_5R'_4)(R''N)MX_2$ ($M=Ti, Zr, Hf$; $X=Cl, Me, R, R', R''=alkyl$) is currently of great scientific and technological interest as a new generation of polymerization catalysts for ethylene, α -olefins and styrene.⁴² As a result, a great number of CGC derivatives have been prepared and tested their polymerization behaviors to understand the structure-property relationship.⁴³

Different from the other metallocene complexes, the dinuclear complex that holds two CGC fragments bonded together through the bridge ligand has been reported. On the basis of our experience in the field of dinuclear metallocene, it has been attempted to synthesize the dinuclear CGC as a new kind of dinuclear metallocene catalyst. This trial has been very fruitful to generate a series of dinuclear constrained geometry catalysts as shown in Scheme VIII.⁴⁴

All dinuclear CGC prepared have been characterized by 1H - and ^{13}C -NMR. The ethylene homopolymerization and ethylene-styrene copolymerization have been carried out with catalyst **24** preliminarily (Table IV).



The detailed information about polymerization behaviors of the dinuclear CGC is not yet available, but some interesting points should be noted based on the above results. The most interesting point is that the activity of dinuclear catalyst **24** increases gradually as the styrene content becomes richer in a reactor. Actually this behavior is just the opposite to Dow CGC. As a consequence, the activity of **24** in ethylene homopolymerization is in the range of 65% of the activity of Dow CGC.

However, the activity of dinuclear CGC in ethylene-styrene copolymerization is getting larger to pass the activity of Dow CGC at styrene content of 100 mL. This represents that the newly synthesized dinuclear CGC catalyzes not only ethylene polymerization but also styrene polymerization very actively. This fact can be clearly demonstrated by measurement of the melting behavior of the generated ethylene/styrene copolymers. As shown in Table IV, the products from **24** have lower melting temperatures than those from the

Table IV. Ethylene/Styrene Copolymerization with Dinuclear CGC **24 and Mononuclear CGC**

Catalyst	C ₂ (psi)	Styrene (mL)	T _p (°C)	Activity (kg Pol/mol · Ti · h)	Styrene content (mol %)	T _m (°C)
24	150	200	70 → 110	6,420	35.9	-
	150	150	70 → 110	6,070	21.2	-
	150	100	70 → 110	5,120	16.0	66
	150	50	70 → 110	4,450	9.8	86
	150	0	70 → 85	3,100	0	-
	150	200	70 → 85	5,550	30.9	-
Mononuclear	150	150	70 → 85	3,500	19.8	-
Dow	150	100	70 → 85	4,050	15.1	69
CGC	150	50	70 → 85	5,100	8.7	91
	150	0	70 → 85	4,800	0	-

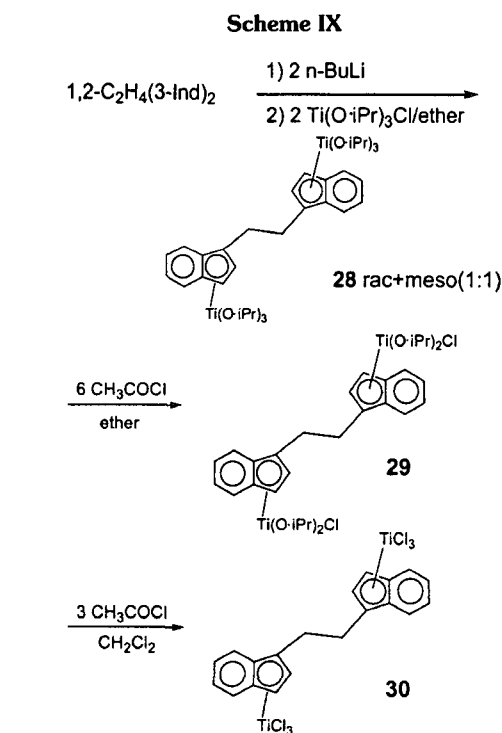
Dow CGC at the identical polymerization conditions. This indicates that styrene reactivity of **24** is superior to that of Dow catalyst. According to ¹³C-NMR study, it turns out that the content of long chain branch in polyethylene from dinuclear catalyst **24** is about 4 to 5 times larger comparing to the polyethylene from mononuclear Dow CGC.

In summary, the dinuclear CGC holding polymethylene bridge exhibits very interesting polymerization behavior. It can polymerize both ethylene and styrene very efficiently to result in the formation of high content of styrene in ethylene/styrene copolymer without difficulty. A continuous effort to elucidate the characteristics of the dinuclear CGC is in progress.

Dinuclear Half-Metallocene

CpTiCl₃ which is the first half-metallocene as a catalyst for the production of syndiotactic polystyrene was introduced by Ishihara and coworkers.⁴⁵ Since then a plenty of studies have been pursued to optimize the polymerization properties with the structural factors of half-titanocene. As a result, the commercial production of syndiotactic polystyrene by Dow and Idemitsu is materialized.⁴⁶ The initial attempt to exploit dinuclear half-metallocene was performed by Royo although he did not pay attention to the polymerization study.^{9,10}

Flores and coworker described the synthesis of the dinuclear half-titanocenes and the effects on activity and syndiospecificity resulting from possible cooperative chemical behavior between the two metal centers.⁴⁷ The synthesis of dinuclear half-



titanocene, 1,2-C₂H₄(1-IndTiCl₃)₂, was achieved through chlorination of the corresponding trialkoxide derivative with acetyl chloride, which had been reported by Nesmeyanov⁴⁸ as shown in Scheme IX.

The polymerization behaviors of the generated dinuclear half-titanocenes, **29**, **30** and mononuclear one, **31**, IndTiCl₃ were tested and the selected data are summarized in Table V.

The activity for the dinuclear half-titanocenes

Table V. Styrene Polymerization Catalyzed by **29**, **30** and **31**

[Ti] (μm)	Al/Ti	T_p ($^{\circ}\text{C}$)	29		30		31	
			Activity	S.I.	Activity	S.I.	Activity	S.I.
25	4,000	25	1,450	94	1,320	80	17,000	92
50	4,000	25	1,000	94	1,200	80	19,000	97
50	4,000	50	1,600	95	1,010	87	37,000	98

Activity : kg of PS/mol Ti \cdot h \cdot mol styrene.S.I. : (g of 2-butanone insoluble polymer/g of bulk polymer) \times 100.

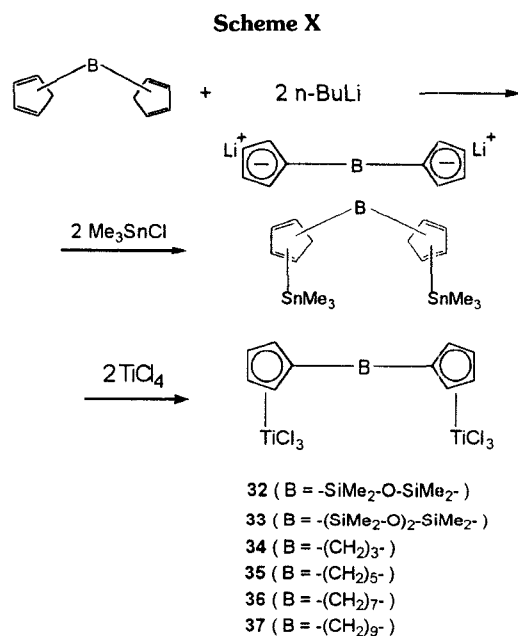
29 and **30** is one order of magnitude lower than that for the mononuclear half-titanocene **31**. However, the syndiospecificities of both dinuclear complexes are comparable to the reference mononuclear complex.

One more interesting feature from their observations is that the purple-black complex **30** in THF turned spontaneously and instantaneously to a clear green-blue solution, from which neither complex **30** nor any other Ti(IV) organometallic-species were detected by ^1H NMR. This observation is in agreement with the behavior of the dinuclear compound $[\mu\text{-}\eta^5\text{:}\eta^5\text{(C}_{10}\text{H}_8\text{)}\text{(TiCl}_3\text{)}_2]$ which decompose to $\text{TiCl}_3(\text{THF})_3$.⁴⁹

Therefore, it is considered that the dinuclear half-titanocenes have a tendency to proceed reductive decomposition inherently. The most important note from this work is that the dinuclear half-metallocenes **29** and **30** are less active than the mononuclear half-metallocene **31**.

An extensive polymerization study for the dinuclear half-titanocene has been exploited by us in recent years.^{21, 24, 27, 28, 30-33, 35} In the same manner that we have tried for the dinuclear Kaminsky-type and constrained geometry catalysts, a series of the dinuclear half-titanocenes with polysiloxane- or polymethylene-bridged ligand have been formed by using distannylated compounds⁵⁰ as shown in Scheme X.

All these complexes **32**–**37** are characterized by spectroscopic tools and employed as styrene



polymerization catalysts in the presence of MMAO.

The polymerization results of polysiloxane-bridged dinuclear half-titanocenes, **32**, **33** and mononuclear one, **38**, CpTiCl_3 are shown in Table VI.

Table VI shows that the dinuclear half-titanocenes with polysiloxane bridges represent lower activities than the corresponding mononuclear half-titanocene. The molecular weight of SPS from the dinuclear half-titanocene is at least 4 times higher than that from the mononuclear one.

Table VI. Results of Styrene Polymerizations Initiated with **32**, **33** and **38**

Catalyst	Activity	S.I. (wt%)	M_w ($\times 10^{-3}$)	M_w/M_n	T_m ($^{\circ}\text{C}$)
32	4.9	97	20	2.0	264
33	12.1	95	25	2.1	263
38	36.9	89	6	1.5	254

[Al]/[Ti] = 1,000.

Activity : kg PS/mol of Ti \cdot h \cdot mol of styrene.

Table VII. Results of Styrene Polymerizations Initiated with 35, 36 and 37

Catalyst	T_p (°C)	[Styrene]	Activity	$M_w (\times 10^{-3})$	M_w/M_n	S.I	T_m (°C)
35	40	1.04	29.4	101	2.8	90	265
35	70	0.35	14.7	21	1.5	60	246
35	70	1.04	52.1	54	2.1	73	261
36	40	1.04	34.7	117	2.4	88	264
36	70	0.35	20.1	31	1.7	61	245
36	70	1.04	59.7	61	2.2	79	258
37	40	1.04	55	130	2.8	91	265
37	70	0.35	114	22	1.6	52	237
37	70	1.04	95	70	2.2	91	260

Activity : kg PS/mol of Ti · h · mol of styrene, [Al]/[Ti]=2,000.

Stereoregularities of SPS produced by the dinuclear catalysts are superior to those of SPS by the mononuclear catalyst. From a standpoint of molecular weight and stereoregularity of the produced SPS, the dinuclear half-titanocene has a big advantage over the mononuclear half-titanocene.

The polymerization results of polymethylene-bridged dinuclear half-titanocenes, **35**, **36** and **37** are shown in Table VII.

In case of polymethylene-bridged compounds, the tendency of low activity in dinuclear half-titanocene seems to remain unless the length of bridges is very long such as nanomethylene. These results are consistent with Flores observation,⁴⁷ as mentioned previously. Among the dinuclear half-titanocene, the longer bridged one displays higher activity than the shorter bridged one regardless of the bridge ligand structure.

In addition, the polymethylene bridge seems to have an advantage over the polysiloxane bridge in terms of catalyst activity.

The activity, molecular weight and stereoregularity of SPS are pretty sensitive to the polymerization conditions. As shown in Table VII, the styrene concentration increase in a reactor improved all the reaction parameters such as activity, molecular weight and stereoregularity. Increasing of polymerization temperature promoted polymerization activity but resulted in dramatic loss of molecular weight and stereoregularity of SPS. A detailed understanding of the above results could not be settled at the moment.

However, it is obvious that the dinuclear half-titanocene has a peculiar characteristics that is different from the normal mononuclear half-

titanocene and this specialty should be resulted from possible cooperative interaction between two centers due to the existence of the bridge ligand. For example, lower activity of the dinuclear half-titanocene might suggest the presence of electron-withdrawing effect by the interaction of two electron-deficient cationic active site. As for the steric effect, it has been proposed that the presence of steric congestion around the active site suppress β -H elimination to result in slowing down the chain termination rate.

With emphasis on the electron effect, it is understandable that the dinuclear catalyst with a long bridge produces a higher molecular weight polymer than the dinuclear one with a short bridge as well as the mononuclear one. In addition, the crowdedness around the metal center will develop the rigidity of active site. The enhanced rigidity of the whole ligand framework would adjust the coordination of styrene monomer to provide a highly stereoregular syndiospecificity of polymer.

Summary

The last decade has been rapid progress in the preparation of new structural metallocene and the understanding of the relation between metallocene structure and polymerization behavior, and the mechanistic principles. The emergency of dinuclear metallocenes was initiated by the intentional effort to make a new kind of metallocene, since it was expected that the dinuclear metallocene would put in extra diversity on catalysis due to the presence of bridge ligand as an additional variable to

adjust metallocene character along with Cp', central metal and anion.

It is clear from the above discussion that the dinuclear metallocene has its own characteristics in polymerization which is not involved in the normal mononuclear metallocene. The plenty studies in which the nature of bridge ligand has been varied have led to significant changes in catalyst activity and polymer property. This has been definitely represented by the remarkable influence observed on the catalyst activity, the molecular weight and stereochemistry of polymer according to change of the structure of dinuclear metallocene. In spite of some important progresses, the development of dinuclear metallocene catalysts has not been concluded and for certain process such as stereoregular polymerization by the dinuclear ansa-metallocene, only temporary optimum values have been reached.

In future, the new dinuclear metallocene with ligand design and reaction conditions will be tailored to bear a predetermined stereoregularity and, to a more extent, a particular catalyst activity or polymer molecular weight.

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