

Preparation of Dinuclear, Constrained Geometry Zirconium Complexes with Polymethylene Bridges and an Investigation of Their Polymerization Behavior

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Abstract: We have prepared the polymethylene-bridged, dinuclear, half-sandwich constrained geometry catalysts (CGC) $[\text{Zr}(\eta^5\text{-C}_9\text{H}_7\text{SiMe}_2\text{NCMe}_3)_2[(\text{CH}_2)_n]$ [$n = 6$ (**9**), $n = 12$ (**10**)] by treating 2 equivalents of ZrCl_4 with the corresponding tetralithium salts of the ligands in toluene. ^1H and ^{13}C NMR spectra of the synthesized complexes provide firm evidence for the anticipated dinuclear structure. In ^1H NMR spectra, two singlets representing the methyl group protons bonded at the Si atom of the CGC are present at 0.88 and 0.64 ppm, which are considerably downfield positions relative to the shifts of 0.02 and 0.05 ppm of the corresponding ligands. To investigate the catalytic behavior of the prepared dinuclear catalysts, we conducted copolymerizations of ethylene and styrene in the presence of MMAO. The prime observation is that the two dinuclear CGCs **9** and **10** are not efficient for copolymerization, which definitely distinguishes them from the corresponding titanium-based dinuclear CGC. These species are active catalysts, however, for ethylene homopolymerization; the activity of catalyst **10**, which contains a 12-methylene bridge, is larger than that of **9** (6-methylene bridge), which indicates that the presence of the longer bridge between the two active sites contributes more effectively to facilitate the polymerization activity of the dinuclear CGC. The activities increase as the polymerization temperature increases from 40 to 70 °C. On the other hand, the molecular weights of the polyethylenes are reduced when the polymerization temperature is increased. We observe that dinuclear metallocenes having different-length bridges give different polymerization results, which reconfirms the significant role that the nature of the bridging ligand has in controlling the polymerization properties of dinuclear catalysts.

Keywords: dinuclear half-sandwich, constrained geometry catalyst, ethylene/styrene copolymerization, polymethylene bridge, zirconium catalyst.

Introduction

The development of a new generation of well-defined group 4 metallocene complexes has made a great impact on the improvement of new polymerization catalysts. It has been found that the metallocene catalyst system has not only exhibited high activity but also revealed the possibility of tailoring the polymer properties such as molecular weight, molecular weight distribution, and stereochemistry.¹⁻⁵ It is believed that these advantages are originated in their well-defined active sites formed by the various structures of ligand and metal, which lead to polymers with specific structures.

After the initial discovery by Kaminsky one of the momentous advances in terms of commercial attention was the appearance of ansa-monocyclopentadienylamido group IV catalysts known as the constrained geometry catalysts (CGC) developed by Dow and Exxon concurrently.⁶⁻⁹ One of the specialties is the highly enhanced copolymerizability of CGC comparing with the normal metallocene catalysts. As a result, these catalysts are very effective to produce long chain branched polyethylenes under the conditions in which vinyl-terminated low molecular polymer generated by β -H elimination or reinserts into the growing polymer chain at the active sites. In addition, these are efficient catalysts not only to perform copolymerization of ethylene with linear α -olefins such as 1-octene but also to incorporate styrene into polyethylene in variable amount.⁹⁻¹⁴

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Recently we have been explored a variety of dinuclear metallocene complexes, which contain two mechanically linked metallocene units via bridges, to study their catalytic properties.¹⁹⁻²² One of the important reasons to pursue these compounds is that dinuclear metallocenes can be a potentially applicable metallocene catalyst for olefin polymerization if two metal centers operate to show cooperative electronic and steric effects on catalytic reaction.¹⁵⁻¹⁸ In reality the previous studies demonstrate well that the dinuclear metallocene catalysts display not only distinguished properties from the known well-defined mononuclear metallocenes, but also a strong dependence of the polymerization behaviors upon the nature of the bridging ligand. It has been suggested that these interactions due to the presence of multicenter active centers may provide high effective reagent local concentrations and consequently enhanced reactivity and selectivity by bringing reactants together via physically or chemical means. On the basis of this idea Mark actually investigated nuclearity effects to observe enhanced polyethylene branching and α -olefin comonomer enchainment in polymerizations mediated by dinuclear CGC with zirconium metal and cocatalysts.¹⁵ More recently, we probed the polymerization properties of dinuclear CGC with titanium metal to observe better styrene incorporation in polyethylene backbone comparing to normal Dow CGC through the ethylene/styrene copolymerizations.²² It has been known that CGC with zirconium exhibited much lower copolymerizability than CGC with titanium metal.^{6,7} Consequently, CGC with zirconium has no use in commercial production of polyethylene copolymers. It would be worth examining the dinuclearity effect of CGC with zirconium metal to enhance copolymerizability of CGC. In this paper we would like to describe the synthesis and polymerization behaviors of new dinuclear CGC with zirconium metal holding polymethylene bridges.

Experimental

General Considerations. All reactions were carried out under a dry, oxygen-free atmosphere using standard Schlenk techniques with a double manifold vacuum line. Nitrogen gas was purified by passage through a column of molecular sieve (4 Å) and Drierite (8 mesh). Tetrahydrofuran, diethyl ether, hexane, toluene, and pentane were distilled from sodium-benzophenone ketyl prior to use. Methylene chloride was distilled from calcium hydride prior to use. 1,6-Dibromohexane and 1,12-dibromododecane purchased from Aldrich were used after distilling from calcium hydride. Modified methylaluminumoxane (MMAO, type 4, 6.4 wt% Al, Akzo, U.S.A.) was used without further purification. ¹H (300 MHz) NMR and ¹³C (75.46 MHz) NMR spectra were recorded using Bruker DPX-300 FT-NMR spectrometer. Mass spectra were performed on a Autospec-Ultima E. IR spectra were recorded on a Jasco FT/IR-5300 spectrophotometer between 4000 and 200 cm⁻¹.

Preparation of [Zr(η^5 : η^1 -C₉H₅SiMe₂NMe₃)Cl₂]₂[(CH₂)₆], 9. A solution of [MeSi(C₉H₅)(NH^tBu)]₂[(CH₂)₆] (2.7 g, 4.71 mmol) in THF 40 mL was treated with 4 equiv. of *n*-BuLi(2.5 M hexane solution, 4 mL, 9.9 mmol) at -78 °C and warmed to 60 °C. After stirring for 12 hrs the resulting orange solution was evacuated to obtain tetralithium salt as a yellow powder in almost quantitative yields (96%). At -78 °C tetralithium salt (2.7 g, 4.52 mmol) in 20 mL toluene was added to the toluene (30 mL) solution of ZrCl₄(3.35 g, 9.04 mmol) dropwisely. The solution was warmed to room temperature to stir for additional 12 hrs. After removing LiCl by filtration the recrystallization of the resulting solution gave the product as a yellow microcrystalline solid(3.31 g, 71%). m.p.: 81 °C; ¹H NMR (300 MHz, 25 °C, CDCl₃): δ 7.71(d, 2H, C₉H₅), 7.62(d, 2H, C₉H₅), 7.40(t, 2H, C₉H₅), 7.26(t, 2H, C₉H₅), 6.31(s, 2H, C₉H₅), 3.02(m, 4H, CH₂), 1.70(m, 4H, CH₂), 1.41(m, 4H, CH₂), 1.33(s, 18H, C(CH₃)₃), 0.88(s, 6H, Si-CH₃), 0.64(s, 6H, Si-CH₃); ¹³C NMR (CDCl₃): δ 138.8, 135.8, 135.0, 128.5, 128.1, 127.9, 127.3, 124.5, 96.7, 63.0, 32.3, 29.7, 29.2, 29.0, 3.3, 1.0. Anal. Calcd. for C₃₆H₅₂N₂Si₂Cl₄Zr₂: C, 48.43%; H, 5.83%; N, 3.14%. Found : C, 48.81%; H, 5.40%; N, 2.72%.

Synthesis of [Zr(η^5 : η^1 -C₉H₅SiMe₂NMe₃)Cl₂]₂[(CH₂)₁₂], 10. This reaction was proceeded in an fashion analogous to that of the above reaction with the following exceptions : [MeSi(C₉H₅)(NH^tBu)]₂[(CH₂)₁₂] (2.45 g, 3.73 mmol) and the corresponding tetralithium salts of this ligand were used in place of [MeSi(C₉H₅)(NH^tBu)]₂[(CH₂)₆], and the tetralithium salt. Recrystallization gave the product as a yellow crystalline (70%). m.p. : 78 °C; ¹H NMR (CDCl₃): δ 7.72(d, 2H, C₉H₅), 7.69(d, 2H, C₉H₅), 7.35(t, 2H, C₉H₅), 7.24(t, 2H, C₉H₅), 6.37(s, 2H, C₉H₅), 2.99(t, 4H, CH₂), 1.68(m, 4H, CH₂), 1.31(s, 18H, C(CH₃)₃), 1.21(m, 16H, CH₂), 0.85(s, 6H, Si-CH₃), 0.59(s, 6H, Si-CH₃); ¹³C NMR (CDCl₃): δ 134.5, 132.1, 130.1, 128.0, 127.6, 126.3, 126.1, 124.3, 91.0, 57.7, 33.5, 30.8, 30.1, 30.0, 29.9, 28.6, 4.6, 2.5. Anal. Calcd. for C₄₂H₆₄N₂Si₂Cl₄Zr₂: C, 51.61%; H, 6.60%; N, 2.87%. Found : C, 50.86%; H, 6.23%; N, 2.49%.

Preparation of Zr(η^5 : η^1 -C₉H₅(*n*-butyl)SiMe₂NMe₃)Cl₂, 11. A solution of butylindenyl(*t*-butylamidodimethyl) silane (2.5 g, 8.29 mmol) in hexanes (50 mL) was treated with 2 equiv. of *t*-BuLi(2.5 M hexane solution, 18.2 mmol) at -78 °C and warmed to RT. After stirring for 24 hrs the resulting milky suspension was filtered to obtain dilithium salt as a yellow powder in almost quantitative yields (96%). At -78 °C dilithium salt (4.25 g, 11.44 mmol) in 50 mL toluene was added to the toluene (50 mL) solution of ZrCl₄(3.5 g, 5.72 mmol) slowly. The solution was warmed to room temperature to stir for additional 12 hrs. After removing LiCl by filtration the recrystallization at -30 °C of the resulting solution gave the product as a yellow microcrystalline solid (3.31 g, 71%). m.p.: 76 °C; ¹H NMR (300 MHz, 25 °C, CDCl₃): δ 7.72(d, 1H, C₉H₅), 7.69(d, 1H, C₉H₅), 7.35(t, 1H, C₉H₅), 7.25(t, 1H, C₉H₅), 6.38(s, 1H, C₉H₅), 3.02(t, 2H,

CH₂), 1.67(m, 2H, CH₂), 1.38(m, 2H, CH₂), 1.31(s, 9H, C(CH₃)₃), 0.93(t, 3H, CH₃), 0.85(s, 3H, Si-CH₃), 0.60(s, 3H, Si-CH₃); ¹³C NMR (CDCl₃): δ 134.5, 132.1, 130.1, 128.0, 127.6, 126.3, 126.1, 124.3, 91.0, 57.6, 33.5, 32.9, 28.3, 23.0, 14.4, 4.6, 2.5. Anal. Calcd. for C₁₉H₂₉NSiCl₂Zr: C, 49.43%; H, 6.33%; N, 3.04%. Found : C, 49.46%; H, 6.62%; N, 3.00%.

Polymerization. Ethylene homopolymerizations and copolymerizations were carried out in a 400 mL glass reactor. The reactor was filled with proper amount of styrene, toluene, and MMAO solution. The system was then saturated with ethylene. With a continuous flow of ethylene the polymerization was initiated by injection of the catalysts and polymerized for 2 hrs. The polymers were precipitated in acidified methanol, filtered, and dried under vacuum to constant weight.

Results and Discussion

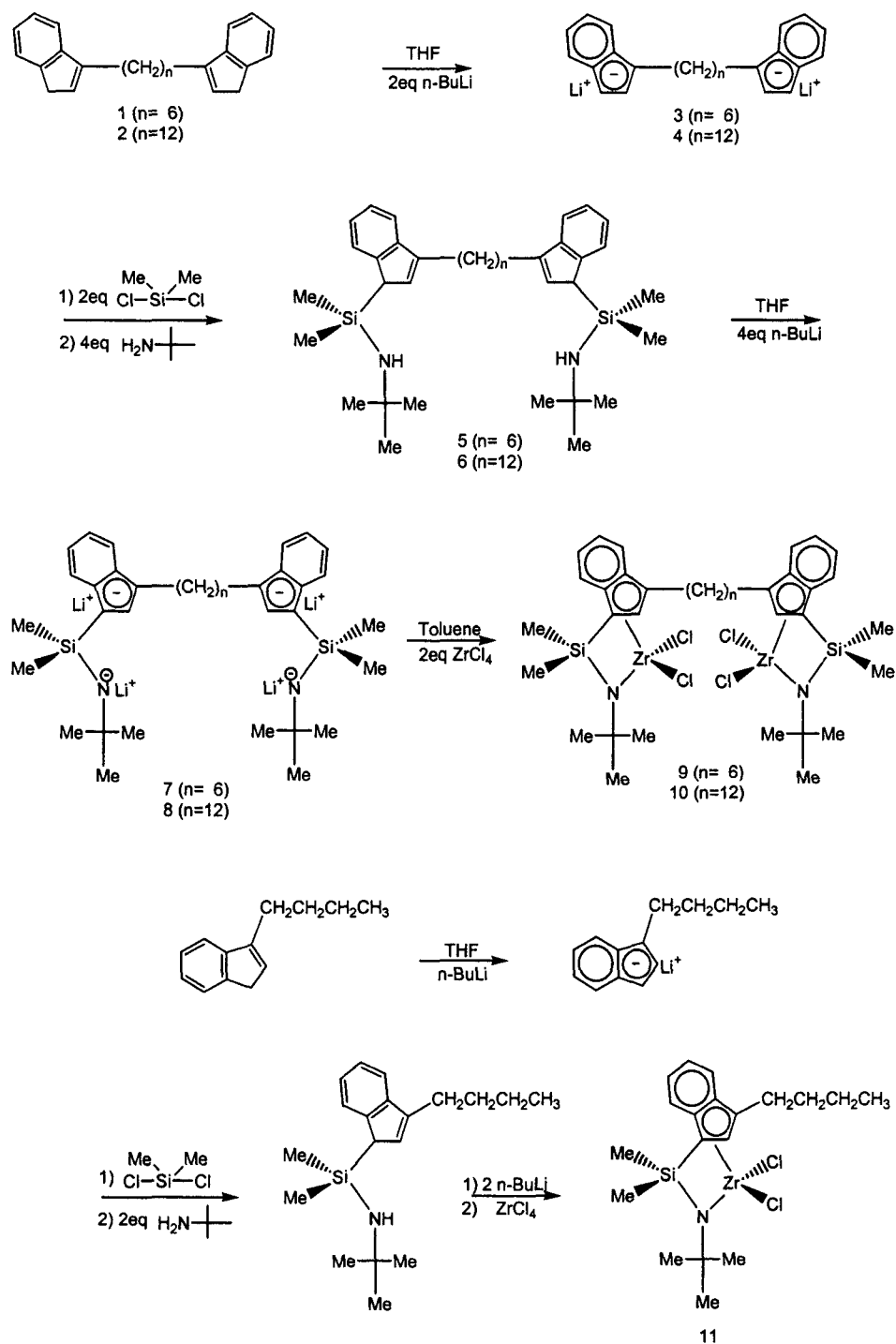
Synthesis and Characterization. Synthesis of polymethylene-bridged dinuclear CGC **9** and **10** with zirconium is achieved by the reaction of tetralithium salts of the corresponding ligands 1,6-bis(dimethyl(tert-butylamino)silylindenyl) hexane, **5**, and 1,12-bis(dimethyl(tert-butylamino)silylindenyl) dodecane, **6**, with two equivalents of ZrCl₄ in toluene at -78 °C followed by warming the solution to room temperature to proceed reaction for 12 hrs (Scheme I). The ligands **5** and **6** were prepared in 90% yields by treatment of the corresponding chloride compounds with four equivalents of *tert*-butylamine in THF for 12 hrs at 60 °C. Yields to obtain the catalysts **9** and **10** have been ranged from 70 to 80% during the metallation step. Contrary to the other examples of the metallation step this process is proved to be very productive to obtain dinuclear CGC in terms of reproducibility as well as yield. Toluene is practically an excellent solvent for the metallation. Better performance of ZrCl₄ in toluene instead of ZrCl₄(THF)₂ in THF for the metallation reagent was not so surprising in the preparation of metallocene complexes with zirconium metals. Dinuclear CGC **9** and **10** are separated as yellow crystalline solids and well soluble in most common organic solvents. ¹H NMR spectra of the complexes **9** and **10** provide firm support for the assigned dinuclear CGC structure. The proton NMR spectra of these compounds are similar to the corresponding titanium-based dinuclear CGC and show two sets of well separated resonances in the aromatic region. The four resonances exhibited between 7.2-7.8 ppm are assigned as the four protons of the six-membered ring in indenyl fragment. Very closely shown two doublets at 7.72 and 7.70 ppm are assigned as the protons at carbons adjacent to 5-membered ring. The two inside protons of 6-membered ring are exhibited at 7.35 and 7.24 ppm due to double coupling with two adjacent protons. The chemical shift at 6.37 ppm as a singlet is due to one proton of the five-membered ring side at indenyl group. Two high field singlets of 0.85 and

0.59 ppm due to two methyls at silicon are very indicative to diagnose the presence of metallated dinuclear complex since these chemical shifts have been shifted to downfield from those at 0.06 and 0.14 ppm of the corresponding ligands **5** and **6**. The ¹³C NMR spectra of the complexes demonstrate the mentioned feature as well. The important point associated with the chemical shift is the downfield chemical shift of 63.0 ppm for **9** and 57.7 ppm for **10** due to the *ipso*-carbon of *t*-butyl group connected at the coordinated nitrogen. Without coordination this carbon of the ligand **5** and **6** normally exhibited around 50 ppm. In contrast the chemical shift of the C1(bridged head) carbon of the indenyl ring is shifted toward highfield from 119 to 97 ppm for **9** and 91 for **10**, respectively. All of these outcomes are in accord with the reported results of both dinuclear and mononuclear CGC with titanium.^{9,13,22} The mononuclear CGC **11** was prepared to compare the polymerization properties with the dinuclear CGC by the reported procedure.

Polymerization. CGC has been recognized as a powerful catalyst when activated with methylaluminoxane(MAO) for the polymerization as well as copolymerization of ethylene.^{6-9,13} On the basis of this knowledge the dinuclear complexes **9** and **10** along with the mononuclear CGC **11** were employed for the polymerization of ethylene and styrene to identify the catalytic characteristics in the presence of MMAO ([Al]/[Zr] ratio of 2,000) at 40 and 70 °C and the results are shown in Table I.

First of all, the effect of the catalyst structure on activity is discussed. The prime feature is that the activity of the mononuclear CGC is much higher than those of the dinuclear CGC. For instance, the catalyst **11** displayed 216 kg polymer/mol. of [Zr].h.atm. of activity at 40 °C which was about 4 times larger than those of the dinuclear catalysts **9** and **10**. Between dinuclear CGC the catalyst **10** having 12 methylenes exhibited larger activity than the catalyst **9** having 6 methylenes. This reconfirms that the dinuclear catalyst with longer bridge between two active sites is able to polymerize ethylene with higher activity than the one with shorter bridge. It is found that polymerization temperature exerts a significant effect on the catalytic activity. In all cases the polymerization temperature increase resulted in activity increase, which is one of the general tendencies shown by the metallocene polymerizations. It is noteworthy that for the catalyst **10** polymerization temperature increase from 40 to 70 °C caused about 3 times activity rise from 91 to 245 kg polymer/mol. of [Zr]. h.atm.. This result may be understood in terms of electronic effects that the more electrons delivered by the presence of longer methylene groups between two metal centers would give more stability to the cationic active sites. This explanation might be valid to discuss the polymerization characteristics of the dinuclear CGC. However, it faces difficulty to rationalize extraordinarily big activity differences between mononuclear and dinuclear CGC since it is hard to believe that difference of the electron releasing effect of *n*-

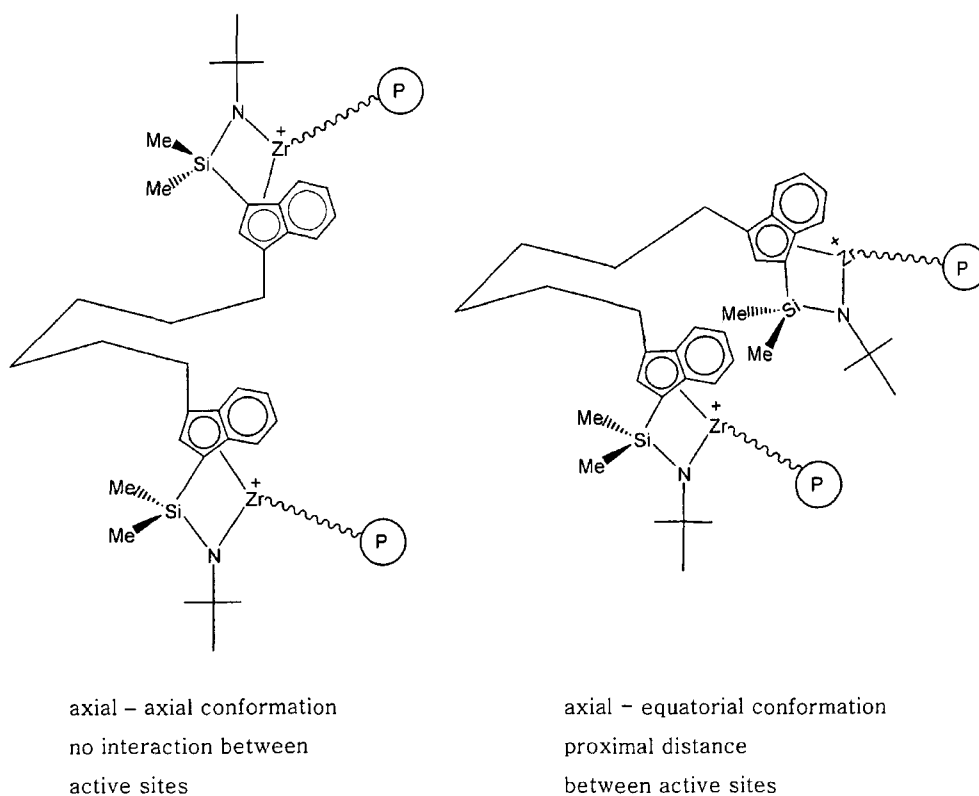
Scheme I



butyl group at the mononuclear catalyst **11** from those of polymethylene bridging groups at the dinuclear CGC **9** and **10** would be responsible for the big activity difference. In addition, we have repeatedly found that the presence of 6 methylenes between two metal centers consistently resulted in the drastic activity reduction of dinuclear metallocenes.

This may give an idea that the steric factor rather than the electronic factor makes more pronounced contribution to derive the polymerization characteristics of the dinuclear CGC. One could propose a contribution of six-membered ring structure as one of the spatial arrangements of the dinuclear CGC with 6 methylene bridge in solution (Scheme

Scheme II



II). Because of bulkiness the structure that two metal complex fragments occupy one equatorial and one axial position in chair shaped conformation could contribute preferentially comparing to the other possible structures. This disposition would provide an opportunity to lie contiguous to the active sites to exert a negative influence on the catalytic activity sterically as well as electronically. On the contrary, the catalyst **10** would be free from this problem because 12 methylene bridge would not form a similar 6-membered ring structure in polymerization system.

One particular thing about the dinuclear catalysts with zirconium is that these are not able to copolymerize ethylene with styrene. As shown in Table I melting points of the generated polymers are ranged from 131 to 136 °C regardless of the monomer composition in feed. This observation demonstrates clearly that all the produced polymers are high density polyethylene and there are no poly(ethylene-*co*-styrene)s. This is completely different result from the dinuclear CGC with titanium.²² It is known that titanium-based dinuclear CGC with polymethylenes were very effective to produce poly(ethylene-*co*-styrene)s with a variable amount of styrene contents. As a matter of fact, zirconium-based CGC was known as a far less efficient catalyst for ethylene-styrene copolymerization than the corresponding CGC with titanium in case of mononuclear CGC.^{6,8} This means that the element of metal in CGC is the most significant single factor to

determine the capability of copolymerization. Consequently, it is believed that a basic copolymerizability property of the catalyst may not be changed by varying the ligand around metal. Instead the change of ligand environment can be useful to make a fine tuning of copolymerizability of CGC. One more thing to be mentioned is that the ethylene homopolymerization activity of CGC with zirconium is much higher than that of CGC with titanium in spite of inferior copolymerization ability of zirconium-based CGC. For instance, the zirconium-based dinuclear CGC **10** with 12 methylene bridge exhibits 245 kg polymer/mol. of [Zr].h.atm. of activity at 70 °C. On the other hand, the activity of the corresponding titanium-based catalyst was 145 kg polymer/mol. of [Ti].h.atm. at same polymerization conditions.

The other feature associated with the activity is that all the catalysts exhibited maximum polymerization activities at the monomer concentration ($[S]/[E] = [\text{styrene}]/[\text{ethylene}]$) ratio of 0, which decreased with increase of the styrene monomer content in feed. The activities of the catalyst **9** and **10** at $[S]/[E] = 0$ were 81 and 245 kg polymer/mol. of [Zr].h.atm at 70 °C, respectively. However, the activities of the same catalysts at $[S]/[E] = 10$ were dropped to 61 and 121 kg polymer/mol. of [Zr].h.atm at 70 °C. This result is not really surprising. It is known that increasing styrene concentration raised the reduction of catalytic activity from the ethylene-styrene copolymerization using CGC.⁹⁻¹³ According to the report this can

Table I. Results of Polymerization with the Catalysts 9, 10 and 11

Catalyst	T_p (°C) ^a	[S]/[E] ^b	Activity ^c	T_m (°C)	M_w ($\times 10^{-4}$)
9	40	0.0	51	135.5	45
		1.0	36	133.7	-
		5.0	28	133.1	34
		10.0	21	134.3	-
	70	0.0	81	132.5	8.5
		1.0	75	130.7	-
		5.0	71	131.4	7.7
		10.0	61	132.2	-
10	40	0.0	91	135.4	41
		1.0	86	135.0	-
		5.0	67	134.7	29
		10.0	55	134.8	-
	70	0.0	245	134.2	6.7
		1.0	199	132.4	-
		5.0	182	133.1	5.4
		10.0	121	134.5	-
11	40	0.0	216	133	58
		1.0	189	133	-
		5.0	134	133	33
		10.0	121	135	-
	70	0.0	256	134	5.1
		1.0	196	133	-
		5.0	140	134	3.6
		10.0	111	134	-

Polymerization conditions: $[Zr] = 2.0 \times 10^{-5}$ mol/L, $[Al]/[Zr] = 2,000$, 2 hr, 1 atm.

^a T_p (°C): polymerization temperature.

^b[S]/[E]: mole ratio of styrene and ethylene.

^cactivity: Kg-polymer/mol. of[Zr].h.atm.

be explained that high concentration of styrene leads to facile reversible deactivation of the active site to a dormant species by additional coordination of styrene due to its additional π -electron system of the phenyl ring. We are positive the adoption of this concept to explain the aforementioned results.

The variation of molecular weight (M_w) with monomer concentration can be illustrated. What we observed is that the use of high styrene concentration is unfavorable to obtain long chain polyethylene. It was found that M_w s of polyethylenes produced without styrene were about at least 30% larger than those of polyethylenes with [S]/[E] = 10. It is understandable that increasing styrene concentration promotes the reversible styrene contact with the active sites to

prevent ethylene coordination. This phenomenon will provide more time to progress β -H elimination of the growing chains in order to produce low molecular weight polymer. As expected, the molecular weight decreased with increasing polymerization temperature drastically ($M_w = 450,000$ at 40°C, **9**; 85,000 at 70°C, **9**; 410,000 at 40°C, **10**; 67,000 at 70°C, **10**; 580,000 at 40°C, **11**; 51,000 at 70°C, **11**). The correlation of molecular weight with the structure of the catalyst did not show a noticeable consistency. At 40°C the mononuclear CGC produced longer polyethylene than the dinuclear CGC. However, at 70°C this tendency has been reversed. This may reflect lower thermal stability of the mononuclear catalyst **11** than the other two. Between the dinuclear CGC the catalyst **9** with 6 methylene bridge produced slightly larger polyethylene than the catalyst **10** with 12 methylene bridge. This indicates that the bridge length influence on the activity of the dinuclear CGC is opposite to that on M_w of the generated polyethylenes by the dinuclear CGC. This is actually very well in accord with the observed results from the studies of the dinuclear zirconocenes.¹⁹⁻²¹

Conclusions

The polymethylene bridged dinuclear half-sandwich CGC (constrained geometry catalyst) $[Zr(\eta^5\text{-}C_9H_5SiMe_2NNMe_3)_2[(CH_2)_n]]$ ($n = 6$ (**9**), $n = 12$ (**10**)) have been successfully prepared by treating 2 equivalents of $ZrCl_4$ with the corresponding tetralithium salts of the ligands. All compounds are separated as yellow brown solids and well soluble in common organic solvents. Proton and Carbon-13 NMR spectra of the synthesized complexes have been very satisfactorily used to characterize the anticipated dinuclear structure. In order to investigate the catalytic behaviors of the prepared dinuclear catalysts copolymerization of ethylene and styrene has been conducted in the presence of MMAO. The prime observation is that the catalyst structure has an important effect on the polymerization properties of the catalysts. It was found that the activity of the mononuclear CGC was much higher than the dinuclear CGC. Between dinuclear CGC the catalyst **10** having 12 methylenes exhibited larger activity than the catalyst **9** having 6 methylenes. This reconfirms that the dinuclear catalyst with longer bridge between two active sites exhibits higher activity than the one with shorter bridge. It is noticeable that the dinuclear catalysts with zirconium were not able to copolymerize ethylene with styrene. This is completely different result from the dinuclear CGC with titanium since titanium-based dinuclear CGC's with polymethylenes were found to be very effective to produce poly(ethylene-co-styrene)s.

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