Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Organometallic Chemistry 667 (2003) 53–60

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Syntheses of dinuclear titanium constrained geometry complexes with polymethylene bridges and their copolymerization properties

Seok Kyun Noh [a,*], Jungmin Lee [a], Dong-ho Lee [b]

[a] *School of Chemical Engineering and Technology, Yeungnam University, 214-1 Daedong, Gyeongsan 712-749, South Korea*
[b] *Department of Polymer Science, Kyungpook National University, Daegu 702-701, South Korea*

Received 31 August 2002; received in revised form 29 October 2002; accepted 31 October 2002

Abstract

The polymethylene bridged dinuclear half-sandwich constrained geometry catalyst (CGC) $[Ti(\eta^5:\eta^1\text{-}C_9H_5SiMe_2NCMe_3)]_2[(CH_2)_n]$ ($n = 6$ (**10**), $n = 9$ (**11**), $n = 12$ (**12**)) have been prepared by treating two equivalents of $TiCl_3(THF)_3$ with the corresponding tetralithium salts of the ligands followed by oxidation by AgCl. Proton and Carbon-13 NMR spectra of the synthesized complexes provide firm evidence for the anticipated dinuclear structure. The important feature associated with the chemical shift of Carbon-13 NMR is the downfield chemical shift of 63.0 ppm due to the *ipso*-carbon of *t*-butyl group bonded at the coordinated nitrogen. In addition the chemical shift of the bridge head carbon at the indenyl ring is shifted toward highfield from 119 to 97 ppm. In order to investigate the catalytic behaviors of the prepared dinuclear catalysts copolymerization of ethylene and styrene was conducted in the presence of modified methylaluminoxane. The prime observance is that their activities increase in the order of **10** < **11** < **12** which indicates the presence of longer bridge between two active sites contributes to facilitate the polymerization activity of the dinuclear CGC. The melting points of the generated copolymers decrease as the styrene portion in feed increases. An interesting point is that styrene content in copolymers formed by the dinuclear catalysts is actually bigger than that in copolymer formed by the mononuclear CGC, which demonstrates the superior comonomer response of the dinuclear CGC comparing to the normal CGC.

Keywords: Dinuclear half-sandwich; Constrained geometry catalyst; Ethylene/styrene copolymerization; Polymethylene bridge

1. Introduction

Since the report of a new generation of Group 4 bent metallocenes containing bridged cyclopentadienyl ligands, appropriate as olefin polymerization catalysts to obtain polyethylenes, and stereoregular polyolefins, there has been increasing interest in the development of the new metallocene-based systems [1–5]. In early days of this decade, a new class of homogeneous Ziegler–Natta catalysts were developed by researchers at Dow [6–8]. These Group 4 mono-cyclopentadienyl-amido catalysts are distinguished by a sterically accessible catalyst active site due to the constrained geometry of the metal center (CGC) [6]. These classes of catalysts are highly active systems producing α-olefin polymers and ethylene/α-olefin copolymers with remarkable properties. This discovery is based on the particular efforts to synthesize cyclopentadienyl ring with a pendant donor group acting as a bidendate ligand bonded to the metal center. While these kinds of catalysts derivatives are easily accessible by various synthetic routes and their polymerization properties have been studied extensively, dinuclear metallocenes holding two metal centers bonded with hetero atoms as one of the ligands to the metal center along with cyclopentadienyl rings have rarely been described. Investigation of the properties of dinuclear metallocenes is interesting, since these metallocenes can serve as a catalyst showing a particular characteristics which could be potentially useful for olefin polymerization if two linked active sites exhibit cooperate electronic and steric influence on catalytic reactions [9–14].

According to the reported studies it is pretty obvious that the dinuclear metallocene systems display not only the distinguished behaviors from the known well-defined mononuclear metallocenes, but also a strong

---

* Corresponding author. Fax: +82-53-814-8790.
E-mail address: sknoh@yumail.ac.kr (S.K. Noh).

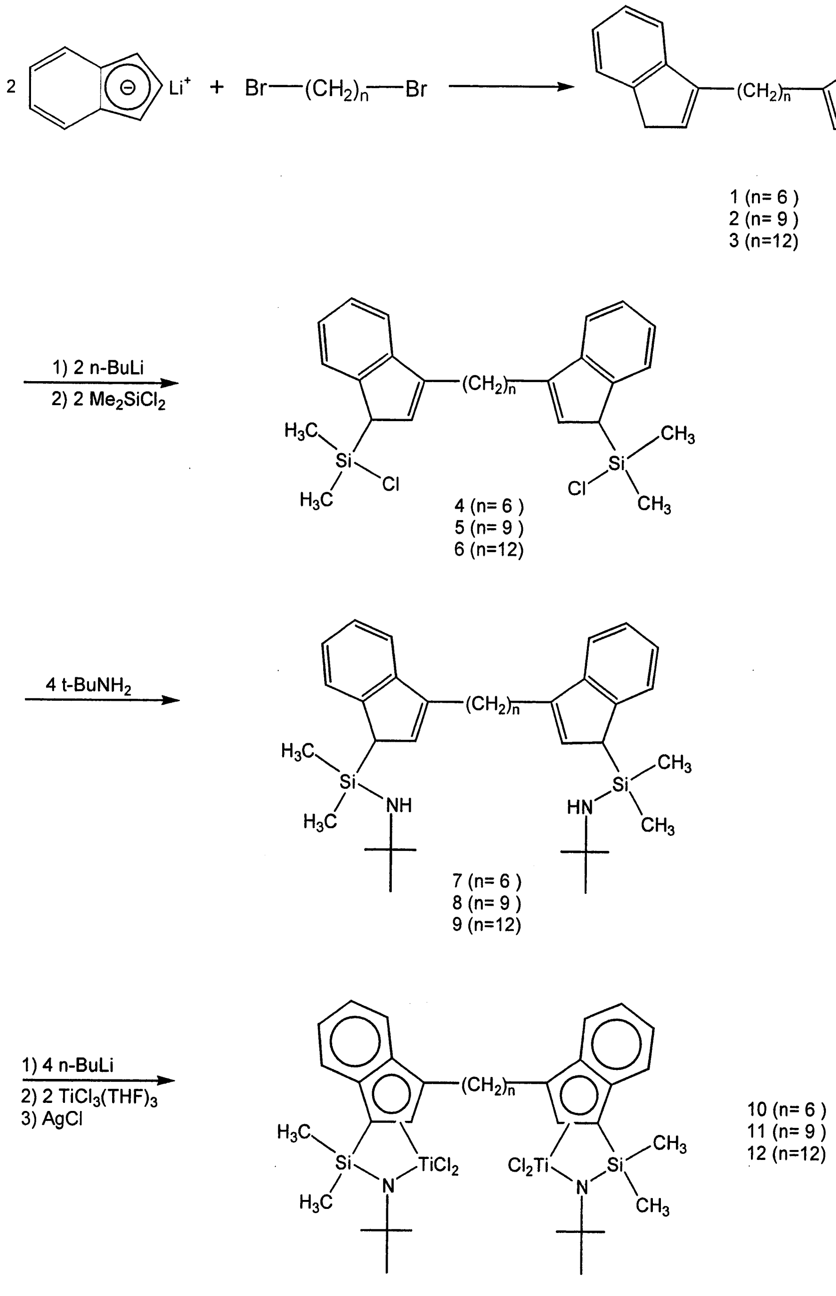
0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(02)02125-3

dependence upon the length as well as the types of the bridge ligand. In this paper we describe the synthesis and ethylene/styrene copolymerization studies of new kinds of dinuclear half-sandwich metallocenes connected with two structurally different bridging ligands.

2. Results and discussion

2.1. Synthesis and characterization

Synthesis of three polymethylene-bridged dinuclear CGC **10**, **11**, and **12** is realized by the reaction of tetralithium salts of the corresponding ligands 1,6-bis(dimethyl(*tert*-butylamino)silylindenyl)hexane **7**, 1,9-bis(dimethyl(*tert*-butylamino)silylindenyl)nonane **8**, and 1,12-bis(dimethyl(*tert*-butylamino)silylindenyl)dodecane **9** with two equivalents of $TiCl_3(THF)_3$ in THF at −78 °C followed by the addition of AgCl after warming the reaction mixture to RT (Scheme 1). The ligands **7**, **8**, and **9** were prepared in 95% yields by treatment of the corresponding chlorides compounds **4**, **5**, and **6** with four equivalents of *tert*-butylamine in THF for 12 h at 60 °C. Use of other metallic salts instead of lithium was found to be unsuccessful for obtaining the desired products. As shown in Scheme 1 the synthetic route is



Scheme 1.

not complicated and applicable to prepare various kinds of dinuclear CGC. One drawback of this procedure is lack of reproducibility in yields that has been ranged from 20 to 75% during the metallation step. THF is practically the only usable solvent for the metallation due to a very poor solubility of TiCl$_3$(THF)$_3$ other than THF. Better performance of TiCl$_3$(THF)$_3$ followed by the oxidation via AgCl instead of the direct introduction of TiCl$_4$ for the metallation reagent to obtain CGC is pretty common and it turned out that in our reaction this concept has also been working satisfactorily [6–8]. All dinuclear CGC's are separated as reddish brown solids and well soluble in most common organic solvents. Since these complexes are very sensitive to moisture they are easily contaminated or decomposed in air exposure. The dinuclear metallocenes **10**, **11**, and **12** are characterized by ^{1}H- and ^{13}C-NMR, IR, and mass spectrometry. ^{1}H-NMR spectra of the complexes **10**, **11**, and **12** provide firm support for the assigned dinuclear CGC structure. The proton NMR spectra of these compound show two sets of well separated resonances in the aromatic region. The four resonances exhibited between 7.2 and 7.8 ppm are assigned as the four protons of the six membered ring in indenyl fragment. The second one that is shown at 6.31 ppm as a singlet is due to one proton of the five membered ring side at indenyl group. The presence of sharp singlet at 1.33 ppm indicated 18 protons of *t*-butyl group bonded to nitrogen. Two highfield singlets of 0.88 and 0.64 ppm due to two methyls at silicon are very indicative to diagnose the presence of metallated dinuclear complexes since it turned out that these chemical shifts have been shifted to downward from the peaks at −0.06 and −0.14 ppm of the corresponding ligand **7**, **8**, and **9**. The resonances of the bridging methylene protons display as three multiplets at 3.02, 1.70, and 1.41 ppm. The ^{13}C-NMR spectra of the complexes demonstrate the mentioned feature well. The important point associated with the chemical shift is the downfield chemical shift of 63.0 ppm due to the *ipso*-carbon of *t*-butyl group connected at the coordinated nitrogen. Without coordination this carbon of the ligand **7**–**9** 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 due to the metal coordination. All of these outcomes are in accord with the reported results of the mononuclear CGC containing indenyl as a Cp' ligand [15–17]. The remaining assignments are summarized in Table 1.

2.2. Polymerization

CGC proved to be powerful catalyst when activated with methylaluminoxane (MAO) for the copolymerization of ethylene and styrene [7,8,17–19]. On the basis of this knowledge the dinuclear complexes **10**, **11**, and **12** were employed for the copolymerization of ethylene and styrene to identify the catalytic characteristics in the presence of modified MAO (MMAO) ([Al]/[Zr] ratio of 2000) at 70 °C and the results are shown in Table 2. From a standpoint of the catalyst activity there are some important points to be noted to differentiate the dinuclear catalysts. The prime feature is that the activity increases sharply as the bridging ligand becomes longer particularly from the complex **10** to **11**. In case of ethylene homopolymerization the activity of the catalysts increases in the order of **10** (21.6 kg of polymer/mol of Ti.h.atm) < **11** (124.8 kg of polymer/mol of Ti.h.atm)

Table 1
Summary of ^{1}H-NMR and ^{13}C-NMR data

Compound	Assignment	^{1}H-NMR	^{13}C-NMR
[Ti(η^5:η^1-C$_9$H$_5$SiMe$_2$NCMe$_3$)Cl$_2$]$_2$[(CH$_2$)$_6$] (**10**)	C$_9$H$_5$	7.71 (d, 8.7 Hz), 7.61 (d, 8.7 Hz)	138.8, 135.8, 135.0
		7.40 (t, 8.4 Hz), 7.26 (t, 8.4 Hz)	128.5, 128.1, 127.9
		6.31 (s)	127.3, 124.5, 96.7
	CH$_2$	3.02 (m), 1.70 (m), 1.41 (m)	29.7, 29.2, 29.0
	t-Butyl	1.33 (s)	63.0 (C$_{ipso}$), 32.0 (CH$_3$)
	Si–CH$_3$	0.88 (s), 0.64 (s)	3.30, 1.0
[Ti(η^5:η^1-C$_9$H$_5$SiMe$_2$NCMe$_3$)Cl$_2$]$_2$[(CH$_2$)$_9$] (**11**)	C$_9$H$_5$	7.71 (d, 8.7 Hz), 7.64 (d, 8.7 Hz)	139.1, 135.8, 135.0
		7.41, (t, 8.5 Hz), 7.27 (t, 8.5 Hz)	129.0, 128.1, 127.9
		6.32 (s)	127.2, 124.5, 96.7
	CH$_2$	2.99 (m), 1.69 (m), 1.41 (br)	30.0, 29.4, 29.3, 29.1
	t-Butyl	1.33 (s)	63.0 (C$_{ipso}$), 32.3 (CH$_3$)
	Si–CH$_3$	0.88 (s), 0.64 (s)	3.40, 1.07
[Ti(η^5:η^1-C$_9$H$_5$SiMe$_2$NCMe$_3$)Cl$_2$]$_2$[(CH$_2$)$_{12}$] (**12**)	C$_9$H$_5$	7.71 (d, 8.7 Hz), 7.62 (d, 8.7 Hz)	139.1, 135.8, 135.0
		7.42, (t, 8.5 Hz), 7.27 (t, 8.5 Hz)	128.5, 128.1, 127.8
		6.32 (s)	127.2, 124.5, 96.6
	CH$_2$	3.00 (m), 1.69 (m), 1.34 (br)	30.0, 29.5, 29.4, 29.3, 29.1
	t-Butyl	1.34 (s)	63.0 (C$_{ipso}$), 32.3 (CH$_3$)
	Si–CH$_3$	0.88 (s), 0.64 (s)	3.38, 1.05

Table 2
Results of ethylene polymerization and ethylene/styrene copolymerization with the dinuclear half-sandwich complexes

Catalyst	[S]/[E] [a]	Activity [b]	T_g (°C)	T_m (°C)
10	0.0	21.6		126.3
	1.0	15.7		99.4
	5.0	11.0	−14.0	
11	0.0	124.8		128.2
	1.0	144.6		91.3
	5.0	97.7	−18.5	
12	0.0	145.5		130.4
	1.0	154.5		108.0
	5.0	120.9	−19.5	

Polymerization condition: $[Ti] = 2.0 \times 10^{-5}$ mol l^{-1}, $[Al]/[Ti] = 2000$.

[a] [S]/[E] = [styrene concentration]/[ethylene concentration].

[b] Activity = kg polymer/mol [Ti].h.atm.

$<$ **12** (145.5 kg of polymer/mol of Ti.h.atm). The tendency has been maintained through the ethylene/styrene copolymerization as shown in Table 2. This behavior is very well in accord with the activity behavior observed on the other dinuclear metallocenes reported by us [12–14]. The second feature is that all the catalysts except the catalyst **10** exhibited maximum polymerization activities at the monomer concentration ([styrene]/[ethylene]) ratio of 1, which decreased with changes of the monomer ratio both above and below this condition. The other comment is the variation of melting temperature of the produced polymers with the ratio of two monomers. What we observed is an anticipated melting point dependence upon the [styrene]/[ethylene] ratio. The T_g and T_m measurement data illustrates clearly that the higher monomer ratio in the feed leads to the formation of the copolymer containing higher content of styrene. From the monomer ratio region of 5 the formed polymers did not show melting temperature instead showed very low T_g of −14 to −20 °C. It is certain that all three catalysts are very efficient to incorporate styrene in polyethylene backbone.

We think these results can be explained by electronic and steric properties of the dinuclear CGC. It is generally accepted that the polymerization activity of the metallocene catalyst increases with increasing electron density at the active center. In our experiments the activity of the catalysts decreased in the order of **12** > **11** > **10**, which demonstrated that the dinuclear catalysts with more [CH_2] units as a bridge represented greater activity. It is not so unreasonable that the more electron density delivered by the adoption of longer polymethylene group as a link between two CGC would stabilize the electron deficient active site to lead the polymerization rate acceleration consequently [12,14]. Bimolecular deactivation process could also be suppressed in connected CGC because of the intramolecular remoteness as well as the intermolecular access disturbance of two active sites. One thing that could be pointed out is the outcome that in spite of the presence of the electron releasing polymethylene bridge, the catalyst **10** displays much lower activity than the other two catalysts **11** and **12**. The difference between the catalyst **10** and the other two may be arisen from the different length of bridges. While the complex **10** has six methylene units as a bridge the others have nine and twelve methylenes respectively as a bridge. We do not have a clear reason why a sudden and steep increase in activity has been observed between the catalyst **10** and **11**. One interpretation we can suppose is that the steric disturbance around the titanium center would prevail to represent the apparent activity of the complex **10** and not electronic effect as a consequence of coming into close contact of two active sites due to the relatively short bridge of six (CH_2) units [14]. On the other hand, the dinuclear CGC holding the bridge longer than six (CH_2) units could be free from this steric disturbance. This result suggests that the length of nine (CH_2) units would correspond to the critical distance, that the electronic effect of the bridge in catalytic properties of the dinuclear CGC surpass the steric hindrance between two active sites.

It is known that increasing styrene concentration decreases catalytic activity [17]. In our experiments the correlation between the activity and the monomer concentration complies with this kind of general tendency. According to the report this can 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 [17–19]. At the [styrene]/[ethylene] ratio of 1 the maximum activity has been consistently observed with the catalysts **11** and **12**. This result might be understood by the comonomer effect which had been observed frequently in ethylene/propylene copolymerization.

In order to test the commercial application of the dinuclear CGC ethylene/styrene copolymerization has been conducted under high pressure (150 psi) condition with the catalyst **11** and Dow CGC and the results are shown in Table 3. The important feature is that the prepared catalyst **11** displays higher activity than Dow CGC at the whole range of copolymerization conditions although this trend has been reversed in ethylene homopolymerization. This suggests the dinuclear complexes could be competitive to produce ethylene copolymer in large scale production. In addition it is worth noting that styrene content in copolymers generated by the dinuclear catalyst is larger than that in copolymer from Dow CGC. This result indicates that comonomer response of the dinuclear catalyst is better than that of the mononuclear CGC. Considering the relative advantages of CGC to the other metallocenes the better

Table 3
Results of ethylene/styrene copolymerization under high ethylene pressure

Catalyst	Ethylene (psi)	Styrene (ml)	Hexane	T_p (°C)	Yield (g)	Activity (kg/mol [Ti].h)	Styrene content (mol%)	T_m (°C)
11	150	200	0	70	64.2	6420	35.9	–
11	150	150	50	70	60.7	6070	21.2	–
11	150	100	100	70	51.2	5120	16.0	66
11	150	50	150	70	44.5	4450	9.8	86
Dow CGC	150	200	0	70	45.5	4550	30.9	–

comonomer response of the catalyst **11** might be a very meaningful characteristics of the dinuclear CGC.

3. Summary

The polymethylene bridged dinuclear half-sandwich constrained geometry catalyst (CGC) $[Ti(\eta^5:\eta^1\text{-}C_9H_5Si\text{-}Me_2NNMe_3)]_2$ $[(CH_2)_n]$ ($n = 6$ (**10**), $n = 9$ (**11**), $n = 12$ (**12**)) have been successfully prepared by treating two equivalents of $TiCl_3(THF)_3$ with the corresponding tetralithium salts of the ligands followed by oxidation by AgCl. All three compounds are separated as reddish brown powder 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. The proton NMR spectra of these exhibit two sets of well separated resonances in the aromatic region. The four peaks shown between 7.2 and 7.8 ppm can easily be assigned as the four protons from the six-membered ring in indenyl ring. The one proton at five-membered ring side of the indenyl is shown at 6.31 ppm as a singlet. The important feature associated with the chemical shift of Carbon-13 NMR is the downfield chemical shift of 63.0 ppm due to the *ipso*-carbon of *t*-butyl group bonded at the coordinated nitrogen. In addition the chemical shift of the bridge head carbon at the indenyl ring is shifted toward highfield from 119 to 97 ppm. 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 observance is that the activity increases in the order of **10** < **11** < **12** which indicates the presence of longer bridge between two active sites contributes to facilitate the polymerization activity of the dinuclear CGC. This result is very well in accord with the activity feature observed on the other dinuclear metallocene catalysts. From the high pressure polymerization experiments it turned out that the activity of the catalyst **11** actually higher than the mononuclear Dow CGC. The melting points of the generated copolymers decrease as the styrene portion in feed increases. An interesting point is that styrene content in copolymers formed by the dinuclear catalysts is actually bigger than that in copolymer formed by the mononuclear CGC, which demonstrates the superior comonomer response of the dinuclear CGC comparing to the normal CGC.

4. Experimental

4.1. 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, 1,9-dibromononane, 1,12-dibromododecane purchased from Aldrich were used after distilling from calcium hydride. MMAO (type 4, 6.4 wt.% Al, Akzo, USA) was used without further purification. ^1H- (300 MHz) NMR and ^{13}C- (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}.

4.2. Preparation of $[Me_2Si(C_9H_6)Cl]_2[(CH_2)_6]$ (**4**)

A solution of Me_2SiCl_2 (1.64 ml, 13.5 mmol) in diethyl ether (20 ml) was cooled to −78 °C and treated dropwise over 15 min with a solution of $[(C_9H_5)_2\text{-}(CH_2)_6]Li_2$ (2.1 g, 6.4 mmol) in ether (50 ml). The resulting solution was warmed to room temperature and stirred for 6 h to obtain yellow suspension solution. Volatiles were then removed in vacuo and the yellowish paste was extracted with hexane. The yellow filtrate was concentrated in vacuo to get the spectroscopically pure products as yellow oil (2.6 g, 80%). ^1H-NMR ($CDCl_3$): δ 7.57 (d, 2H, C_9H_6), 7.44 (d, 2H, C_9H_6), 7.31 (t, 2H, C_9H_6), 7.22 (t, 2H, C_9H_6), 6.30 (s, 2H, C_9H_6), 3.63 (s, 2H, allylic indene-H), 2.62 (t, 4H, CH_2), 1.71 (m, 4H, CH_2), 1.47 (m, 4H, CH_2), 0.21 (s, 6H, Si–CH_3), 0.18 (s, 6H, Si–CH_3); ^{13}C-NMR ($CDCl_3$): δ 144.8, 144.3, 143.5, 127.2, 125.4, 124.2, 123.3, 119.2, 45.4, 29.5, 28.5, 27.7, 0.02, −0.28.

4.3. Preparation of $[\mathrm{Me_2Si(C_9H_6)(NH^tBu)}]_2[(\mathrm{CH_2})_6]$ (7)

A solution of $[\mathrm{Me_2Si(C_9H_6)Cl}]_2[(\mathrm{CH_2})_6]$ (**4**, 2.6 g, 5.2 mmol) in THF (50 ml) was treated with *tert*-butylamine (2.46 ml, 23.4 mmol) via syringe. The resulting suspension was warmed to 60 °C and stirred overnight. Volatiles were removed in vacuo, and the pale yellow paste was extracted with hexane (20 ml × 3). The yellow filtrate was concentrated in vacuo to get the product as orange oil (2.7 g, 91%). ^{1}H-NMR ($\mathrm{CDCl_3}$): δ 7.59 (d, 2H, $\mathrm{C_9H_6}$), 7.47 (d, 2H, $\mathrm{C_9H_6}$), 7.30 (t, 2H, $\mathrm{C_9H_6}$), 7.22 (t, 2H, $\mathrm{C_9H_6}$), 6.39 (s, 2H, $\mathrm{C_9H_6}$), 3.53 (s, 2H, allylic indene-H), 2.68 (t, 4H, $\mathrm{CH_2}$), 1.78 (m, 4H, $\mathrm{CH_2}$), 1.55 (m, 4H, $\mathrm{CH_2}$), 1.25 (s, 18H, $\mathrm{C(CH_3)_3}$), 0.69 (s, 2H, NH), 0.02 (s, 6H, Si–$\mathrm{CH_3}$), −0.05 (s, 6H, Si–$\mathrm{CH_3}$); ^{13}C-NMR ($\mathrm{CDCl_3}$): δ 146.0, 144.7, 141.6, 130.3, 124.3, 123.2, 118.8, 49.5, 46.6, 33.8, 29.6, 28.7, 27.7, −0.01, −0.92.

4.4. Synthesis of $[\mathrm{Ti}(\eta^5{:}\eta^1\text{-}\mathrm{C_9H_5SiMe_2NCMe_3})\mathrm{Cl_2}]_2[(\mathrm{CH_2})_6]$ (**10**)

A solution of $[\mathrm{Me_2Si(C_9H_6)(NH^tBu)}]_2[(\mathrm{CH_2})_6]$ (**7**, 2.7 g, 4.71 mmol) in THF 40 ml was treated with four equivalents 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 h the resulting orange solution of the tetralithium salt was cooled to −78 °C. $\mathrm{TiCl_3(THF)_3}$ (3.35 g, 9.04 mmol) in THF 30 ml was added to the solution of the teralithium salt at −78 °C dropwisely. The black brown solution was warmed to room temperature to stir for additional 3 h. AgCl (1.3 g, 9.0 mmol) was added as a solid, and silver mirror precipitated immediately. THF was removed in vacuo after 30 min and the residue was extracted with toluene. After filtering and removing toluene the residue was extracted with hexane. Recrystallization of the resulting solution gave the product as reddish brown solid (1.79 g, 48%). ^{1}H-NMR ($\mathrm{CDCl_3}$): δ 7.71 (d, 2H, $\mathrm{C_9H_5}$), 7.62 (d, 2H, $\mathrm{C_9H_5}$), 7.40 (t, 2H, $\mathrm{C_9H_5}$), 7.26 (t, 2H, $\mathrm{C_9H_5}$), 6.31 (s, 2H, $\mathrm{C_9H_5}$), 3.02 (m, 4H, $\mathrm{CH_2}$), 1.70 (m, 4H, $\mathrm{CH_2}$), 1.41 (m, 4H, $\mathrm{CH_2}$), 1.33 (s, 18H, $\mathrm{C(CH_3)_3}$), 0.88 (s, 6H, Si–$\mathrm{CH_3}$), 0.64 (s, 6H, Si–$\mathrm{CH_3}$); ^{13}C-NMR ($\mathrm{CDCl_3}$): 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. High-resolution mass spectrum: [$\mathrm{P^+}$] $\mathrm{C_{36}H_{52}N_2Si_2Cl_4Ti_2}$, $m/z = 804$ ([$\mathrm{M^+}$], 15%), 769 ([$\mathrm{M^+}$]−Cl, 30%).

4.5. Preparation of $[\mathrm{Me_2Si(C_9H_6)Cl}]_2[(\mathrm{CH_2})_9]$ (**5**)

A solution of $\mathrm{Me_2SiCl_2}$ (1.81 ml, 14.3 mmol) in diethyl ether (20 ml) was cooled to −78 °C and treated dropwise over 15 min with a solution of $[(\mathrm{C_9H_5})_2(\mathrm{CH_2})_9]\mathrm{Li_2}$ (2.26 g, 14.3 mmol) in ether (50 ml). The resulting solution was warmed to room temperature and stirred for 6 h to obtain yellow suspension solution. Volatiles were then removed in vacuo and the yellowish paste was extracted with hexane. The yellow filtrate was concentrated in vacuo to get the spectroscopically pure products as yellow oil (3.38 g, 94%). ^{1}H-NMR ($\mathrm{CDCl_3}$): δ 7.59 (d, 2H, $\mathrm{C_9H_6}$), 7.47 (d, 2H, $\mathrm{C_9H_6}$), 7.33 (t, 2H, $\mathrm{C_9H_6}$), 7.24 (t, 2H, $\mathrm{C_9H_6}$), 6.33 (s, 2H, $\mathrm{C_9H_6}$), 3.65 (s, 2H, allylic indene-H), 2.64 (t, 4H, $\mathrm{CH_2}$), 1.70 (m, 4H, $\mathrm{CH_2}$), 1.37 (m, 10H, $\mathrm{CH_2}$), 0.24 (s, 6H, Si–$\mathrm{CH_3}$), 0.22 (s, 6H, Si–$\mathrm{CH_3}$); ^{13}C-NMR ($\mathrm{CDCl_3}$): δ 144.8, 144.4, 143.5, 127.2, 125.4, 124.2, 123.3, 119.3, 45.4, 29.6, 29.5, 28.0, 27.7, 0.03, −0.27.

4.6. Preparation of $[\mathrm{Me_2Si(C_9H_6)(NH^tBu)}]_2[(\mathrm{CH_2})_9]$ (**8**)

A solution of $[\mathrm{MeSi(C_9H_5)Cl}]_2[(\mathrm{CH_2})_9]$ (**5**, 3.38 g, 6.2 mmol) in THF (50 ml) was treated with *tert*-butylamine (2.95 ml, 27.9 mmol) via syringe. The resulting suspension was warmed to 60 °C and stirred overnight. Volatiles were removed in vacuo, and the pale yellow paste was extracted with hexane (20 ml × 3). The yellow filtrate was concentrated in vacuo to get the product as orange oil (3.68 g, 96%). ^{1}H-NMR ($\mathrm{CDCl_3}$): δ 7.53 (d, 2H, $\mathrm{C_9H_6}$), 7.41 (d, 2H, $\mathrm{C_9H_6}$), 7.25 (t, 2H, $\mathrm{C_9H_6}$), 7.16 (t, 2H, $\mathrm{C_9H_6}$), 6.32 (s, 2H, $\mathrm{C_9H_6}$), 3.47 (s, 2H, allylic indene-H), 2.60 (t, 4H, $\mathrm{CH_2}$), 1.69 (m, 4H, $\mathrm{CH_2}$), 1.40 (m, 10H, $\mathrm{CH_2}$), 1.20 (s, 18H, $\mathrm{C(CH_3)_3}$), 0.64 (s, 2H, NH), −0.03 (s, 6H, Si–$\mathrm{CH_3}$), −0.01 (s, 6H, Si–$\mathrm{CH_3}$); ^{13}C-NMR ($\mathrm{CDCl_3}$): δ 146.0, 144.8, 141.7, 130.3, 124.2, 123.2, 118.8, 49.5, 46.6, 34.0, 29.7, 29.5, 28.8, −0.01, −0.94.

4.7. Synthesis of $[\mathrm{Ti}(\eta^5{:}\eta^1\text{-}\mathrm{C_9H_5SiMe_2NCMe_3})\mathrm{Cl_2}]_2[(\mathrm{CH_2})_9]$ (**11**)

A solution of $[\mathrm{Me_2Si(C_9H_6)(NH^tBu)}]_2[(\mathrm{CH_2})_9]$ (**8**, 3.68 g, 5.98 mmol) in THF 40 ml was treated with four equivalents of *n*-BuLi (2.5 M hexane solution, 10.7 ml, 26.9 mmol) at −78 °C and warmed to 60 °C. After stirring for 12 h the resulting orange solution of the tetralithium salt was cooled to −78 °C. $\mathrm{TiCl_3(THF)_3}$ (4.06 g, 10.9 mmol) in THF 30 ml was added to the solution of the teralithium salt at −78 °C dropwisely. The black brown solution was warmed to room temperature to stir for additional 3 h. AgCl (1.57 g, 11 mmol) was added as a solid, and silver mirror precipitated immediately. THF was removed in vacuo after 30 min and the residue was extracted with toluene. After filtering and removing toluene the residue was extracted with hexane. Recrystallization of the resulting solution gave the product as reddish brown solid (3.37 g, 73%). ^{1}H-NMR ($\mathrm{CDCl_3}$): δ 7.71 (d, 2H, $\mathrm{C_9H_5}$), 7.64 (d, 2H,

C_9H_5), 7.41 (t, 2H, C_9H_5), 7.27 (t, 2H, C_9H_6), 6.32 (s, 2H, C_9H_5), 2.99 (m, 4H, CH_2), 1.69 (m, 4H, CH_2), 1.41 (m, 10H, CH_2), 1.33 (s, 18H, $C(CH_3)_3$), 0.88 (s, 6H, Si–CH_3), 0.64 (s, 6H, Si–CH_3); ^{13}C-NMR ($CDCl_3$): δ 139.1, 135.8, 135.0, 128.1, 127.9, 127.2, 124.5, 96.7, 63.0, 32.3, 30.0, 29.4, 29.3, 29.1, 3.40, 1.07. High-resolution mass spectrum: [P^+] $C_{39}H_{58}N_2Si_2Cl_4Ti_2$, $m/z = 846$ ([M^+], 13%), 811 ([M^+]–Cl, 35%).

4.8. Preparation of [$Me_2Si(C_9H_6)Cl]_2[(CH_2)_{12}]$ (**6**)

A solution of Me_2SiCl_2 (1.81 ml, 14.3 mmol) in diethyl ether (20 ml) was cooled to −78 °C and treated dropwise over 15 min with a solution of $[(C_9H_5)_2(CH_2)_{12}]Li_2$ (2.5 g, 6.8 mmol) in ether (50 ml). The resulting solution was warmed to room temperature and stirred for 6 h to obtain yellow suspension solution. Volatiles were then removed in vacuo and the yellowish paste was extracted with hexane. The yellow filtrate was concentrated in vacuo to get the spectroscopically pure products as yellow oil (3.38 g, 94%). ^{1}H-NMR ($CDCl_3$): δ 7.57 (d, 2H, C_9H_6), 7.45 (d, 2H, C_9H_6), 7.31 (t, 2H, C_9H_6), 7.22 (t, 2H, C_9H_6), 6.29 (s, 2H, C_9H_6), 3.62 (s, 2H, allylic indene-H), 2.61 (t, 4H, CH_2), 1.71 (m, 4H, CH_2), 1.36 (m, 6H, CH_2), 1.28 (br, 10H, CH_2), 0.20 (s, 6H, Si–CH_3), 0.19 (s, 6H, Si–CH_3); ^{13}C-NMR ($CDCl_3$): δ 144.8, 144.4, 143.5, 127.1, 125.4, 124.2, 123.3, 119.3, 45.4, 29.6, 29.5, 28.5, 27.7, 0.04, −0.31.

4.9. Preparation of [$Me_2Si(C_9H_6)(NH^tBu)]_2[(CH_2)_{12}]$ (**9**)

A solution of $[MeSi(C_9H_5)Cl]_2[(CH_2)_{12}]$ (**6**, 3.38 g, 6.2 mmol) in THF (50 ml) was treated with *tert*-butylamine (2.95 ml, 27.9 mmol) via syringe. The resulting suspension was warmed to 60 °C and stirred overnight. Volatiles were removed in vacuo, and the pale yellow paste was extracted with hexane (20 ml × 3). The yellow filtrate was concentrated in vacuo to get the product as orange oil (3.68 g, 96%). ^{1}H-NMR ($CDCl_3$): δ 7.50 (d, 2H, C_9H_6), 7.38 (d, 2H, C_9H_6), 7.23 (t, 2H, C_9H_6), 7.14 (t, 2H, C_9H_6), 6.30 (s, 2H, C_9H_6), 3.45 (s, 2H, allylic indene-H), 2.57 (t, 4H, CH_2), 1.66 (m, 4H, CH_2), 1.36 (m, 6H, CH_2), 1.26 (br, 10H, CH_2), 1.17 (s, 18H, $C(CH_3)_3$), 0.61 (s, 2H, NH), −0.06 (s, 6H, Si–CH_3), −0.14 (s, 6H, Si–CH_3); ^{13}C-NMR ($CDCl_3$): δ 146.0, 144.8, 141.7, 130.3, 124.2, 123.2, 123.0, 118.8, 49.5, 46.5, 33.8, 29.8, 29.7, 29.5, 28.8, 27.7, −0.03, −0.94.

4.10. Synthesis of [$Ti(\eta^5:\eta^1$-$C_9H_5SiMe_2NCMe_3)Cl_2]_2[(CH_2)_{12}]$ (**12**)

A solution of $[Me_2Si(C_9H_6)(NH^tBu)]_2[(CH_2)_{12}]$ (**9**, 2.45 g, 3.73 mmol) in THF 40 ml was treated with four equivalents of *n*-BuLi (2.5 M hexane solution, 6.71 ml, 16.8 mmol) at −78 °C and warmed to 60 °C. After stirring for 12 h the resulting orange solution of the tetralithium salt **9** was cooled to −78 °C. $TiCl_3(THF)_3$ (2.42 g, 6.53 mmol) in THF 30 ml was added to the solution of **9** at −78 °C dropwisely. The black brown solution was warmed to room temperature to stir for additional 3 h. AgCl (0.89 g, 6.22 mmol) was added as a solid, and silver mirror precipitated immediately. THF was removed in vacuo after 30 min and the residue was extracted with toluene. After filtering and removing toluene the residue was extracted with hexane. Recrystallization of the resulting solution gave the product as reddish brown solid (1.51 g, 55%). ^{1}H-NMR ($CDCl_3$): δ 7.71 (d, 2H, C_9H_5), 7.65 (d, 2H, C_9H_5), 7.42 (t, 2H, C_9H_5), 7.27 (t, 2H, C_9H_5), 6.32 (s, 2H, C_9H_5), 3.00 (t, 4H, CH_2), 1.69 (m, 4H, CH_2), 1.34 (m, 4H, CH_2), 1.33 (s, 18H, $C(CH_3)_3$), 1.23 (m, 10H, CH_2), 0.88 (s, 6H, Si–CH_3), 0.64 (s, 6H, Si–CH_3); ^{13}C-NMR ($CDCl_3$): δ 139.1, 135.8, 135.0, 128.5, 128.1, 127.8, 127.2, 124.5, 96.6, 63.0, 32.3, 30.0, 29.5, 29.4, 29.3, 29.1, 3.38, 1.05. High-resolution mass spectrum: [P^+] $C_{42}H_{64}N_2Si_2Cl_4Ti_2$, $m/z = 888$ ([M^+], 16%), 853 ([M^+]–Cl, 36%).

4.11. Polymerization

4.11.1. Under one atmosphere ethylene pressure reactions

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 h. The polymers were precipitated in acidified methanol, filtered, and dried under vacuum to constant weight.

4.11.2. Under 150 psi ethylene pressure reactions

In a 2 l autoclave were introduced sequentially the proper amount of hexane, styrene, and MAO solution. After heating the reactor to the polymerization temperature the catalyst solution was injected into the reactor followed by the pressurizing the reactor with ethylene immediately, so that an in situ start of the polymerization was achieved. The polymers were treated and separated as the same procedures as mentioned above.

Acknowledgements

We are grateful to the Yeungnam University Research grant in 2001 for financial support.

References

[1] G.G. Hlatky, Chem. Rev. 100 (2000) 1347.

[2] S. Mecking, Coord. Chem. Rev. 203 (2000) 325.

[3] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169.

[4] H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143.

[5] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. Engl. 38 (1999) 428.

[6] A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587.

[7] J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Rosen, G.W. McKnight, S. Lai, Eur. Pat. Appl. 0416815A2 (1991).

[8] J.C. Stevens, D.R. Neithamer, Eur. Pat. Appl. 0418044A2 (1991).

[9] D.H. Lee, S.K. Noh, Korea Polym. J. 9 (2001) 71.

[10] W. Spaleck, F. Kuber, B. Bachmann, C. Fritz, A. Winter, J. Mol. Cat. A: Chem. 128 (1998) 278.

[11] K. Soga, H.T. Ban, T. Uozumi, J. Mol. Cat. A: Chem. 128 (1998) 273.

[12] S.K. Noh, S. Kim, J. Kim, D.H. Lee, K.B. Yoon, H.B. Lee, S.W. Lee, W.S. Huh, J. Polym. Sci. Part A: Polym. Chem. 35 (1997) 3717.

[13] S.K. Noh, J. Kim, J. Jung, C.S. Ra, D.H. Lee, H.B. Lee, S.W. Lee, W.S. Huh, J. Organomet. Chem. 580 (1999) 90.

[14] J. Jung, S.K. Noh, D.H. Lee, S.K. Part, H.J. Kim, J. Organomet. Chem. 595 (2000) 147.

[15] A.L. McKnight, R.M. Waymouth, Macromolecules 32 (1999) 2816.

[16] F. Amor, J. Okuda, J. Organomet. Chem. 520 (1996) 245.

[17] F.G. Sernetz, R. Mülhaupt, F. Amor, T. Eberle, J. Okuda, J. Polym. Sci. Part A: Polym. Chem. 35 (1997) 1571.

[18] T. Arai, T. Ohtsu, S. Suzuki, Macromol. Rapid Commun. 19 (1998) 327.

[19] G. Xu, Macromolecules 31 (1998) 2395.