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Articles

Polymerization of 1,3-Butadiene Catalyzed by Half-Sandwich Titanocenes Bearing a Coordinative Ether and Ester Side Chain on the Cp Ring and MAO[†]

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ABSTRACT: Substituted half-titanocenes bearing coordinative ether and ester moiety in their side chains, η^5:η^1-$C_5H_4(CH_2CH_2OMe)TiCl_3$ (**5b**), η^5-$C_5H_4(CH_2CH_2CH_2OMe)TiCl_3$ (**5c**), and η^5:η^1-$C_5H_4(CH_2COOMe)$-$TiCl_3$ (**5d**), were prepared, and then their catalytic performances for the stereospecific living polymerization of 1,3-butadiene in the presence of the methylaluminoxane (MAO) were investigated. The introduction of intramolecular coordination between central titanium and the ether or ester moiety (**5b**,**d**) caused acceleration of polymer propagation rate and enhancement of cis-specificity. The catalyst **5d**/MAO showed 114 times larger propagation rate constant than that of the parent nonsubstituted η^5-$C_5H_5TiCl_3$ (**5f**)/MAO catalyst. The **5b**/MAO catalyzed 1,3-butadiene polymerization gave high *cis*-polybutadiene (99.2% cis content) with narrow molecular weight dispersity (1.14). The single-crystal X-ray crystallographic analysis of **5d** and reaction pathway are also discussed.

Introduction

This decade has seen a tremendous increase in the number of reports on conjugated diene polymerization with a catalytic system composed of a transition metal complex and methylalumoxane (MAO) or a combination of noncoordinative borate compounds and aluminum alkyl (borate/R_3Al). In 1,3-butadiene polymerization, one research interest is to develop a new catalytic system that simultaneously controls both polymer microstructure, especially a cis-1,4-structure, and a narrow molecular weight distribution (M_w/M_n, MWD) which will improve mechanical and thermal properties such as toughness, impact strength, clarity, and haze of the resulting polybutadienes.[1] Although the conventional heterogeneous Ziegler−Natta type catalysts are powerful tools for promoting stereospecific polymerizations of conjugated dienes in high levels, control of molecular weight is very limited.[2] Very recently, promising reports obtained polybutadienes with more than 95% *cis*-1,4-structure and a relatively narrow MWD less than 2.0, when using homogeneous lanthanide (Sm[3] and Nd[4]) based complexes and CoL_2 (L = F, Cl, Br, I)[5] in the presence of MAO or borate/R_3Al as an activator. Under certain conditions, some of these catalysts promote living polymerization to give relatively narrow MWD (<2.0).

We reported that titanium based half-metallocenes with various types of alkyl substituent on the cyclopentadienyl ring with MAO catalyst are able to promote living polymerizations of 1,3-butadiene to afford an extremely narrow MWD (=1.04).[6] However the content of the *cis*-1,4-structure in the resulting polybutadiene was 93.5% at best, and the *cis*-1,4-content strongly depends on the bulkiness and electron-donating character of substituents.

Herein we report a novel catalytic system composed of titanium based half-metallocenes with a substituent that coordinative ether and carbonyl units on the cyclopentadienyl ring with MAO in 1,3-butadiene polymerization. This is the first examples of a titanium based catalysts with a high *cis*-1,4-specificity and a narrow MWD for 1,3-butadiene polymerization.

Results and Discussion

Synthesis and Structure of Cyclopentadienyltitanium Complexes. Half-sandwich titanocenes η^5:η^1-$C_5H_4(CH_2CH_2OMe)TiCl_3$ (**5b**),[7] η^5-$C_5H_4(CH_2CH_2CH_2$-$OMe)TiCl_3$ (**5c**), η^5:η^1-$C_5H_4(CH_2COOMe)TiCl_3$ (**5d**), and $\{[\eta^5$:η^1-$C_5H_4(CH_2CH_2)O]TiCl_2\}_2$ (**5e**)[8] were synthesized

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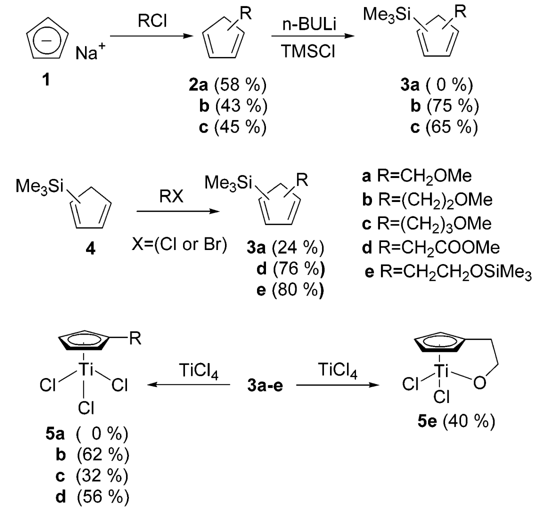
Scheme 1



by slightly modifying a method previously reported in the literature. Scheme 1 depicts the synthetic route for the above half-sandwich titanocenes with coordinative ether and carbonyl moieties. Substituted cyclopentadienes **2a**−**c** were prepared by reacting sodium cyclopentadienide with the corresponding chloromethoxyalkanes to give methoxymethyl-,[9] methoxyethyl-,[10] and methoxypropylcyclopentadiene (**2a**−**c**) in 58, 43 and 45% yield, respectively. The TMS group in the cyclopentadienyl ring of **2a**−**c** was introduced by lithiation and subsequent trimethylsilylation to give the desired disubstituted cyclopentadienes (**3b**,**c**) in 75 and 65%, respectively. Unfortunately, for **2a** only byproducts, *n*-pentylcyclopentadiene and *n*-pentyltrimethylsilylcyclopentadiene were obtained. Therefore, the desired **2a** was prepared from trimethylsilylcyclopentadiene via lithiation−alkylation process. The alkylations of **4** were performed by reacting the lithium salt generated by lithiation of **4** and chloromethyl methyl ether, methyl bromoacetate and 2-chloroethyl trimethylsilyl ether to give desired ethers (**3a**,**d**) and ester (**3e**) in 24, 76 and 80% yield, respectively. Complexation of the intermediates **3a**−**e** with $TiCl_4$ conducted at −78 °C under an Ar atmosphere gave trichlorocyclopentadienyltitanium complexes (**5b**−**e**) in 62, 32, 56 and 40%, respectively. However, the preparation of **5a** was unsuccessful; only tar-like materials were obtained.

Complexes **5b**−**e** have a coordinative side chain. For **5b** and **5e**, the existence of an intramolecular coordination between central titanium and ether oxygen in solution and solid state was already confirmed by NMR and single-crystal X-ray crystallographic analysis.[7] Complex **5c** was obtained as yellow oil at room temperature, which could not be recrystallized as pure materials due to the high solubility in common solvent. Thus, solid-state molecular structure determination of **5c** could not be conducted by X-ray analysis. The protons attached to cyclopentadienyl ring **5c** appeared as two sets of triplet at 6.8−6.9 ppm, which was very similar to half-sandwich titanocenes with an alkyl group on the cyclopentadienyl ring, while the methyl protons in the methoxy group appeared as singlet at 3.3 ppm. This chemical shift was same as that for intermediate **3c**. Moreover, significant changes were not observed in variable temperature NMR measurements. These results indicate that the ether moiety of **5c** does not coordinate to the central titanium in solution. On the other hand, the same NMR analysis for complex **5d** showed a singlet signal for the protons on the cyclopentadienyl ring and lower field shifted methyl protons for the methoxy group. These characteristic phenomena are very similar to those of known **5b** and strongly suggest the existence of intramolecular coordination between the central titanium and carbonyl oxygen in solution.

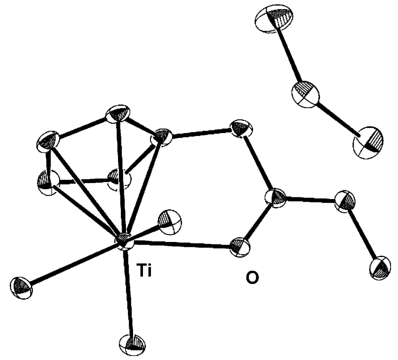


Figure 1. Molecular structure of **5d**.

Table 1. Crystal Data for 5d

diffractometer	Rigaku AFC-7R
empirical formula	$C_9H_8O_2Cl_5Ti$
fw	373.33
cryst color, habit	orange, prismatic
cryst dimens	0.30 × 0.30 × 0.30 mm
cryst syst	triclinic
lattice params	$a = 7.944(2)$ Å
	$b = 12.386(3)$ Å
	$c = 7.812(3)$ Å
	$\alpha = 100.33(2)°$
	$\beta = 99.30(3)°$
	$\gamma = 73.52(2)°$
	$V = 720.2(4)$ Å^3
space group	$P1$ (No. 2)
Z value	2
D_{calc}	1.721 g/cm^3
μ(Mo Kα)	15.05 cm^{-1}
F (000)	370.00
temp	−80 °C
no. of reflcns	3549 (measd)
	3312 (unique)
	3216 (obsd)
R, R_w	0.041, 0.067

Fractional recrystallization of **5d** from CH_2Cl_2 produced a good crystalline for single-crystal X-ray analysis. Figure 1 depicts the ORTEP drawing, and the crystal data are shown in Table 1. The intramolecular coordination between the central titanium and carbonyl oxygen was observed in solid state. Compared to the structural feature of **5b**, the bond length of Ti1−O1 was shorter (2.182(2) Å) than that of **5b** (2.217(10) Å). Significant aspects of other features for bond lengths, bond angles, and dihedral angles were not observed. This suggests the molecular structure of **5d** is almost the same as **5b**.

Polymerization of 1,3-Butadiene. Table 2 summarizes the results of 1,3-butadiene polymerizations catalyzed by **5b**−**e** at +25 and −25 °C. The **5b**−**e**/MAO catalysts promoted the 1,3-butadiene polymerizations; in particular, the **5d**/MAO catalyst showed extremely high catalytic activity. In all cases except for catalyst **5e**/MAO, the GPC curves of polybutadienes prepared by the catalysts at 25 °C showed monomodal shapes with relatively narrow MWDs. Although the catalytic activities naturally decreased, the MWDs of polymers became narrower when the polymerizations were conducted at −25 °C. The GPC curves of polybutadienes

Table 2. Results of 1,3-Butadiene Polymerizations Catalyzed with 5b−e/MAO[a]

run	complex	temp (°C)	time (h)	yield (%)	$M_n{}^b \times 10^{-4}$	$M_w/M_n{}^b$	microstructure[c]		
							cis-	*trans-*	1,2-
1	**5b**	25	1	44.3	19.6	1.89	97.7	0.8	1.5
2	**5b**	−25	20	59.3	62.0	1.14	99.2	0	0.8
3	**5c**	25	3	36.0	13.0	2.84	78.6	4.6	16.8
4	**5c**	−25	140	24.1	28.3	1.24	83.7	3.0	13.3
5	**5d**	25	0.25	92.0	9.6	2.41	93.0	2.0	5.0
6	**5d**	−25	0.25	48.0	24.9	1.09	95.0	0	5.0
7	**5e**	25	7	43.0	*d*		87.7	1.5	11.8
8	**5e**	−25	24	5.1	*d*		88.2	2.4	9.4

[a] Conditions: $[\mathrm{BD}]_0 = 6.0-7.0$ wt % in toluene, $[\mathrm{BD}]_0/[\mathrm{Ti}] = 100$ g/mol, and [Al]/[Ti] = 1000. [b] Determined by GPC and calibrated with polybutadiene standards. [c] Determined by ^{1}H and ^{13}C NMR. [d] Broad bimodal.

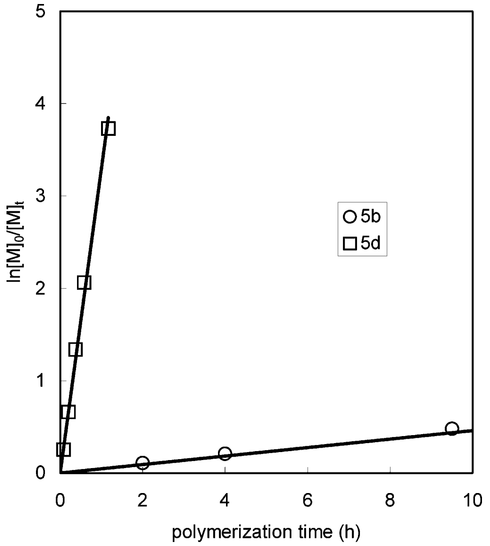


Figure 2. First-order plots of 1,3-butadiene polymerization catalyzed by **5b**,**d**/MAO at −25 °C. Polymerization conditions are described in Table 2.

prepared by **5e**/MAO showed bimodal shapes. This indicates that at least two types of active species are generated by the reaction of **5e** and MAO. The use of the catalyst **5e** having a covalent titanium−oxygen bond is less effective for the cis-specific polymerization of 1,3-butadiene. Therefore, the polymerizations using **5b**,**d**/MAO catalysts were kinetically analyzed. As shown in Figure 2, first order plots gave satisfactory linear relationship, which indicates that the number of active reaction sites is constant and a termination reaction like a chain transfer reaction is negligible. The number-averaged molecular weight of polybutadienes obtained proportionally increased as the polymer yield increased. (Figure 3) The MWDs of polybutadienes were in a narrow range during the course of polymerization. These results suggest the **5b**,**d**/MAO catalysts can promote 1,3-butadiene polymerization with a living character.

To achieve a detailed understanding of the living character of the active catalysts **5b**,**d**/MAO, the initiator efficiencies (IE) and propagation rate constants (k_p) by the catalysts **5b**−**d**/MAO at −25 °C were estimated according to a literature method.[6b] (Table 3) Introducing a coordinative side chain decreased the IEs for the catalysts **5b**,**d**/MAO, but propagation rate constants larger than those for the parent unsubstituted half-titanocene **5f** and alkyl substituted half-titanocenes **5g** were observed. When the polymerizations catalyzed by **5f**/MAO were conducted under the same condition in the presence of methyl acetate as an additive (1.0 and 10.0 equiv), significant differences were not observed in the catalytic activity and stereospecificity. This indicates that intramolecular coordination between central titanium and coordinative ether and ester units plays an important role in accelerating propagation. Figure 4 shows the postpolymerization result. The GPC profile of polybutadiene obtained during first polymerization (100% yield) moved to a higher molecular weight region along with a narrow MWD (second polymerization, 195% yield). From this result, it was determined that the **5d**/MAO catalyst promotes the living polymerization of 1,3-butadiene at −25 °C.

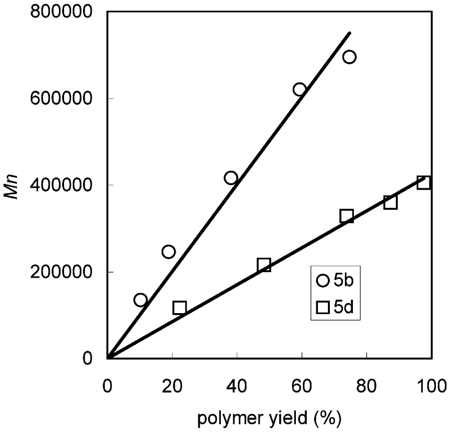


Figure 3. M_n and MWD vs polymer yields plots for 1,3-butadiene polymerization initiated by **5b**,**d**/MAO catalysts at −25 °C. Polymerization conditions are the same as Figure 2.

Table 3. Initiator Efficiencies (IE) and Propagation Rate Constants (k_p)[a]

entry	catalysts	IE (%)	k_p (L mol^{-1} min^{-1})
1	**5b**/ MAO	13.8	13.2
2	**5c**/MAO	8.0	0.9
3	**5d**/ MAO	30.2	332
4[b]	η^5- $C_5H_5TiCl_3$ (**5f**)/MAO[b]	56.6	2.9
5[b]	η^5- $C_5H_4(n\text{-Bu})TiCl_3$ (**5g**)/MAO[b]	51.3	3.0

[a] Polymerization conditions were the same as Table 1. [b] See ref 6b.

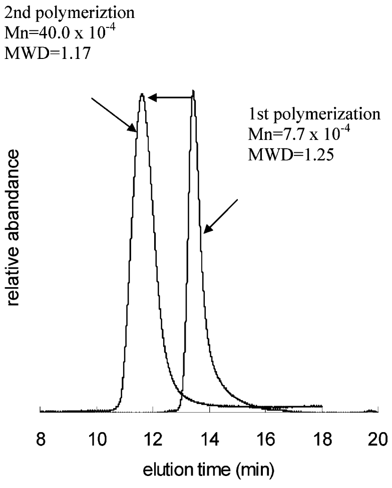


Figure 4. GPC profiles of polybutadienes obtained in post-polymerization catalyzed by **5d**/MAO at −25 °C

Microstructure Analysis. Table 2 lists the microstructure distribution (cis-, trans- and 1,2-) of polybutadienes obtained in this research. ^{13}C NMR was used to determine the microstructure.[6b,11] Although the cata-

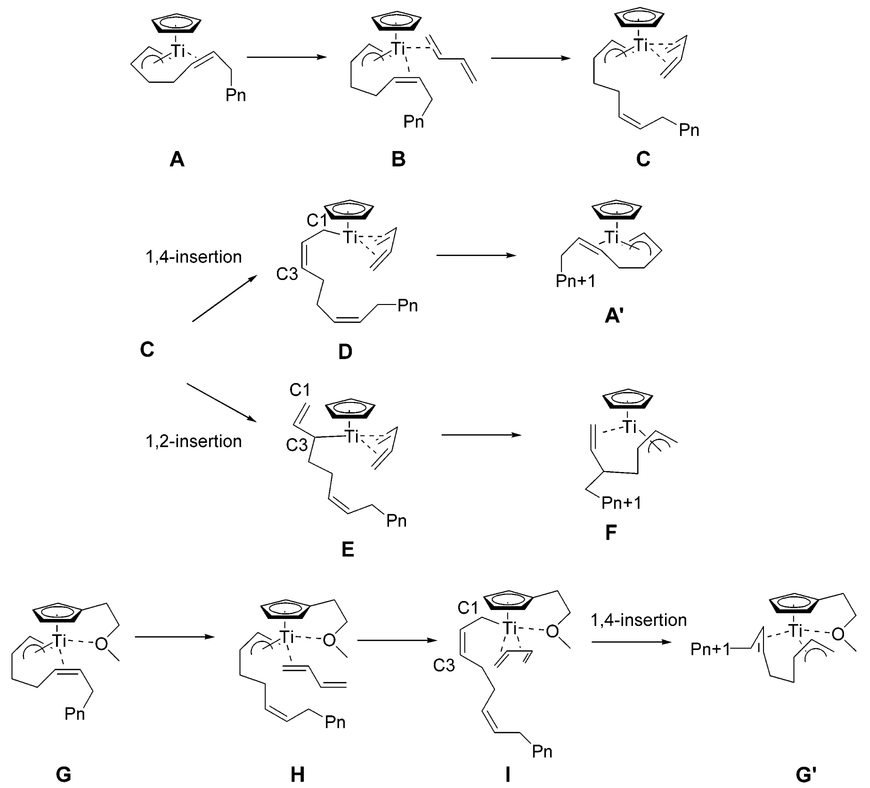


Figure 5. Plausible reaction mechanism of 1,3-butadiene polymerization catalyzed by **5b**/MAO.

lysts in this study showed a remarkable ligand effect on cis-selectivity, all the polybutadienes obtained at +25 and −25 °C exhibit a predominantly cis structure. Especially, catalysts **5b**,**d/MAO** showed extremely high cis-selectivity (99.2% of cis content for **5b**, 95.0% for **5d**) and trans units were negligible at −25 °C. Using the parent unsubstituted complex **5f**, alkyl substituted **5g**, and noncoordinative methoxypropyl substituted **5c** did not significantly enhance the cis-selectivity. Apparently, intramolecular coordination also plays an important role to enhanced cis-selectivity.

The reason for the high cis-selectivity caused by the intramolecular coordination between the central titanium and coordinative side chain in the **5b**,**d**/MAO catalysts is unclear. However, Figure 5 shows a plausible mechanism based on the experimental and theoretical considerations of Porri and Peluso.[2,12] They proposed the following reaction mechanism. (1) The rate-determining step is the coordination of incoming 1,3-butadiene to the active central titanium. (2) The central titanium is a cationic titanium species. (3) The structure of the active species in half-titanocene/MAO catalyzed 1,3-butadiene polymerization is composed of π-allyl titanium and a backbiting double bond derived from the former inserted 1,3-butadiene unit. (4) The backbiting interaction stabilizes the polymer chain end π-allyl unit as an anti-form, which is a key intermediate for controlling the polymer main chain cis structure.

According to the polymerization mechanism mentioned above, the rate-determining step is the coordination of an incoming monomer to the active catalytic species (**A**) with the simultaneous switching of growing polymer chain coordination mode from π-allyl (**C**) to σ-allyl (**D**, **E**) structure. Then the insertion processes to produce active species **A′** and **F** from the intermediates **D** and **E** occur to give 1,2- or 1,4-butadiene insertion unit, respectively.

In the presence of a coordinative side chain on the cyclopentadienyl ring, a lone pair on the oxygen atom in the ether and ester groups would coordinate toward cationic central titanium to form intermediate **G** during the course of 1,3-butadiene polymerization. An incoming thermally stable s-*trans*-1,3-butadiene coordinates to the cationic central titanium while kicking out the backbiting double bond to form intermediate **H**. The coordinated 1,3-butadiene isomerizes to the bidentate s-*cis*-conformer, in harmony with the π-allyl changing to the σ-allyl species at the polymer chain end. The resulting intermediate **I** is converted to **G′**, an analogue of **G**, by the insertion of coordinated 1,3-butadiene. The presence of oxygen atom that coordinates to central titanium should make easier the switching from π-allyl to σ-allyl, thus improving the propagation rate. Moreover the oxygen atom coordinated to central titanium should increase the σ-allyl coordination mode of the growing polymer chain thus favoring the formation of *cis*-1,4 units, in fact when the growing polymer chain is π-allyl bonded, the incoming monomer can insert at C1 or C3 of the allylic unit, intermediate **C**, with formation of 1,4- or 1,2-units, respectively.

Conclusion

We demonstrated half-titanocenes with coordinative ether and ester side chains, η^5:η^1−$C_5H_4(CH_2CH_2OMe)$-$TiCl_3$ (**5b**) and η^5:η^1−$C_5H_4(CH_2COOMe)TiCl_3$ (**5d**), can promote high cis-selective living polymerization of 1,3-butadiene in the presence of MAO. Polymerization temperature strongly influences the polymerization activity and cis-selectivity in this catalytic system. A low-temperature polymerization provides high *cis*-polybutadiene with narrow MWD. The intramolecular coordination between ether and ester units introduced at side chain and central titanium plays a key role to enhancing polymerization activity and stereoselectivity.

Experimental Section

General Remarks. All melting and boiling points are uncorrected.

Chemicals. The MAO toluene solution purchased from Tosoh-Fine-Chem. Co. Ltd., was used without further treatment. All solvents used for reactions were dried in the general manner and were distilled prior to use. Other chemicals purchased were used without further purification. 1,3-Butadiene and isoprene (>99.5% purity) donated from Nippon Zeon Co., Ltd., were purified by drying distillation in the presence of a small portion of MAO prior to use for polymerization.

Analysis. Gel permeation chromatographic analyses to determine molecular weight and MWD for polymers were performed on a Tosoh HLC8020 system with THF as eluent at 40 °C using polybutadiene and polystyrene standard samples for calibration. NMR spectra were recorded at 600 MHz for ^{1}H nuclei and 150 MHz for ^{13}C nuclei on a Nippon Denshi Lambda 600 spectrometer, and the signal of nondeuterated chloroform was used as internal reference. High-resolution mass spectra (HRMS) were obtained on a Hitachi M-80B spectrometer at 75 eV using a direct inlet system. Single-crystal X-ray crystallographic analysis was performed on Rigaku AFC-7R diffractometer.

Typical Procedure for the Alkylation of Cyclopentadiene. To a solution of 16.1 mL (200 mmol) of chloromethylmethyl ether in 100 mL of hexane was added dropwise 50 mL (100 mmol) of sodium cyclopentadienide (2.0 M THF solution) at 0 °C with stirring under argon atmosphere. After addition was completed, the resulting reaction mixture was stirred for 5 h at room temperature. The reaction was quenched by addition of a small amount of methanol and was poured into a large amount of ice/water. The organic materials were extracted with hexane several times. The hexane extract was washed with water and brine, was dried over magnesium sulfate, and then was concentrated to leave a residue. The residue was distilled under reduced pressure to give 6.0 g (58% yield based on sodium cyclopentadienide) of methoxymethylcyclopentadiene (**2a**) as isomeric mixture: colorless liquid; bp 45 °C (20 mmHg) (lit.[9] bp 75−78 °C (65 mmHg)).

Compounds **2b**−**c** were prepared in a similar manner.

Methoxyethylcyclopentadiene (2b) (isomeric mixture): colorless liquid; bp 30 °C (5 mmHg) (lit.[7a] bp 40 °C (40 mmHg)).

Methoxypropylcyclopentadiene (2c) (isomeric mixture): colorless liquid; bp 48−51 °C (4 mmHg); ^{1}H NMR ($CDCl_3$) δ ppm 6.4−6.0 (3H, m), 3.38 (2H, m), 3.32 (3H, s), 2.92 (2H, d), 2.46 (2H, m), 1.81 (2H, m); HRMS calculated for $C_9H_{14}O$ 138.1044, found 138.1042.

Typical Procedure for the Trimethylsilylation of 2a—c. To a solution of 2.95 g (28 mmol) of **2a** in mixed solution of 48 mL of dry hexane and 12 mL of dry THF was added dropwise 18.7 mL (30 mmol) of *n*-BuLi (1.6 M hexane solution) at −78 °C with stirring under argon atmosphere. After addition was completed, the reaction mixture was allowed to stir for 1 h at room temperature. Then the reaction mixture was cooled to −78 °C, and 3.8 mL (30 mmol) of chlorotrimethylsilane was added dropwise via syringe to the reaction mixture. The resulting mixture was warmed to room temperature and stirred for 1 h. A small amount of methanol was added to the reaction mixture to quench the reaction. The reaction mixture was concentrated to leave a residue. The residue was purified by distillation under reduced pressure to give *n*-pentylcyclopentadiene (20%) as a first fraction (57−58 °C (6 mmHg)) and *n*-pentyl(trimethylsilyl)cyclopentadiene (36%) as a second fraction (86−88 °C (5 mmHg)).

***n*-Pentylcyclopentadiene:** colorless liquid; ^{1}H NMR ($CDCl_3$) δ ppm 6.6−5.9 (3H, m), 2.93 (2H, (d) 2.40 (2H, m), 1.58 (2H, m), 1.35 (4H, m), 0.93 (3H, t).

***n*-Pentyl(trimethylsilyl)cyclopentadiene:** colorless liquid; ^{1}H NMR ($CDCl_3$) δ ppm 6.6−5.9 (3H, m), 2.93 (1H, (d) 2.40 (2H, m), 1.54 (2H, m), 1.32 (4H, m), 0.93 (3H, t), −0.03 (9H, s).

Compounds **3b**,**c** were prepared in a similar manner.

Methyloxyethyl(trimethylsilyl)cyclopentadiene (3b, isomeric mixture): colorless liquid; bp 66−68 °C (4 mmHg) (lit.[7b] 66−68 °C (4 mmHg)).

Methoxypropyl(trimethylsilyl)cyclopentadiene (3c, isomeric mixture): colorless liquid; bp 54−56 °C (1 mmHg); ^{1}H NMR ($CDCl_3$) δ ppm 6.7−5.9 (3H, m), 3.38 (2H, t, $J = 6.6$ Hz), 3.33 (3H, s), 3.23 (1H, s), 2.45 (2H, t, $J = 6.6$ Hz), 1.81 (2H, quin, $J = 6.6$ Hz), −0.06 (9H, s); HRMS calculated for $C_{12}H_{22}OSi$ 210.1440, found 210.1430.

Typical Procedure for the Alkylation of Trimethylsilylcyclopentadiene (4). To a solution of 8.0 g (57.8 mmol) of trimethylsilylcyclopentadiene (**4**) in mixed solution of 10 mL of dry hexane and 100 mL of dry THF was added dropwise 26.3 mL (63.6 mmol) of *n*-BuLi (1.6 M hexane solution) at −78 °C with stirring under argon atmosphere. After the addition was completed, 4.6 mL (60.7 mmol) of chloromethylmethyl ether was added dropwise to the resulting pale yellow solution at −78 °C. The reaction mixture was stirred for additional 1 h at room temperature and quenched by the addition of a small amount of methanol. The reaction mixture was poured into a large amount of ice/water and extracted with hexane several times. The organic phase was separated, dried over magnesium sulfate and concentrated to leave a residue. The residue was purified by vacuum to give 2.5 g of methoxymethyl-(trimethylsilyl)cyclopentadiene (**3a)** as an isomeric mixture in 24% yield: colorless prisms; bp 35−38 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) δ ppm 6.8−6.1 (3H, m), 4.26 (2H, s), 3.36 (3H, s), 3.03 (1H, s), −0.03 (9H, s); HRMS calculated for $C_{11}H_{18}OSi$ 182.1123, found 182.1140.

Compounds **3d**,**e** were prepared in a similar manner.

Methoxycarbonylmethyl(trimethylsilyl)cyclopentadiene (3d, isomeric mixture): colorless liquid; bp 54 °C (1 mmHg), ^{1}H NMR ($CDCl_3$) δ ppm 6.55−6.20 (3H, m), 3.69 (2H, s), 3.67 (3H, s), 3.15 (1H, m), −0.04 (9H, s).

Trimethylsilyloxyethyl(trimethylsilyl)cyclopentadiene (3e, isomeric mixture): colorless liquid; bp 59 °C (2 mmHg) (lit.[8] bp 40 °C (40 mmHg)).

Typical Procedure for the Complexation Reaction of 3b—e with $TiCl_4$. To a solution of 3.23 g (16.5 mmol) of **3b** in 60 mL of dichloromethane was added carefully 1.7 mL (15.5 mmol) of $TiCl_4$ via syringe at −78 °C under argon atmosphere. Then the colorless solution turned clear orange immediately. The resulting orange solution was stirred for 1 h and evaporated to leave a residue. The resulting orange solid was recrystallized from dichloromethane to give orange crystals: trichloro(methoxyethylcyclopentadienyl)titanium (**5b**); orange prisms (CH_2Cl_2); mp 91 °C (lit.[7a] mp 92−94 °C).

Compounds **5c**−**e** were prepared in a similar manner.

η^5-$C_5H_4(CH_2CH_2CH_2OMe)TiCl_3$ (5c): yellow needles at −20 °C; ^{1}H NMR ($CDCl_3$) δ 6.92 (2H, t, $J = 2.5$ Hz), 6.84 (2H, t, $J = 2.5$ Hz), 3.41 (2H, t, $J = 6.0$ Hz) 3.33 (3H, s), 2.94 (2H, t, $J = 7.6$ Hz), 1.93 (2H, t, $J = 7.6$ Hz).

η^5:η^1-$C_5H_4(CH_2COOMe)TiCl_3$ (5d): orange prisms (CH_2Cl_2); mp 78−79 °C; ^{1}H NMR ($CDCl_3$) δ 7.00 (4H, s), 3.92 (2H, s), 3.76 (3H, s). Anal. Calcd for $C_8H_9O_2TiCl_3$: Ti, 18.47. Foun: Ti, 18.92.

$\{[\eta^5$:η^1-$C_5H_4(CH_2CH_2)O]TiCl_2\}_2$ (5e): orange needles; mp 179 °C (lit.[8] mp 177−178 °C)

Typical Procedure for the Polymerization of 1,3-Butadiene with Half-Titanocene/MAO Catalyst. Aging Process. To a solution of 9.3 mL of MAO (28.3 mmol of Al) in toluene solution was added slowly via syringe a solution of 0.0283 mmol of η^5-$C_5H_4(CH_2CH_2OCH_3)TiCl_3$ in 0.67 mL of dry toluene. The resulting mixture was aged for 5 min at room temperature, and then that solution was cooled to −25 °C before addition to monomer solution.

Polymerization. Polymerization was carried out using 150 mL of pressure resistant glass ampule equipped with rubber septum. To a solution of 2.83 g (28.3 mmol) of BD in 36 mL of dry toluene solution was added the above aged catalyst solution at once via syringe at −25 °C, and polymerization was conducted for the stated time at −25 °C. The clear monomer solution turned pale green immediately. Polymerization was terminated by addition of a small amount of acidic methanol containing 2,6-di-*tert*-butyl-*p*-cresol (1 wt %) as antioxidant reagent, and the resulting polymer solution was poured into a large amount of above methanol solution. Then the crude bulk polymer was precipitated and collected. The crude polymer was dissolved again in toluene and the catalyst ash was removed by centrifugation. Purified polymer was reprecipitated by pouring into a large amount of above methanol, collected, and dried under reduced pressure in vacuo at 60 °C for 12 h.

X-ray Crystallographic Analysis of 5d. The details of X-ray data collection, lattice parameter, and physical properties of the crystal **5d** are summarized in Table 1. Lattice parameters were determined for a crystal mounted in a Lindeman glass capillary from 25 reflections in the range $29.77° < 2\theta < 30.03°$. The structure was solved by direct methods (SIS92). Full-matrix least-squares refinement was performed on F^2 with all non-hydrogen atoms anisotropic and hydrogen in calculated positions with $U_{iso,}$ = 2.08 times of U (bonded atoms). The weighting scheme was $w = 1/[\sigma^2 (F_0^2)]$. Final R and R_w values were 0.041 and 0.067 (refined on F^2).

References and Notes

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