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Carbazolyl-Substituted [OSSO]-Type Zirconium(IV) Complex as a Precatalyst for the Oligomerization and Polymerization of α-Olefins

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Abstract: The dibenzyl zirconium(IV) complex (**4**) incorporating with a carbazolyl(Cbz)-substituted [OSSO]-type bis(phenolate) ligand was synthesized. Upon activation with dried modified methylaluminoxane (dMMAO), precatalyst **4** at relatively low catalyst loadings was found to promote the 1,2-regioselective oligomerization of 1-hexene to produce the corresponding vinylidene-ended oligomers with moderate turnover frequencies (TOFs) up to 2080 h^{-1}. The ^{13}C NMR analysis of the resulting oligomers revealed the formation of dimer-enriched oligo(1-hexene)s in 39–62% distributions. The precatalyst **4** with dried methylaluminoxane (dMAO) also exhibited good performance in the polymerization of styrene yielding isotactic polystyrenes ([*mm*] > 99%) with quite large molecular weights (M_w < 508,100 g mol^{-1}) and relatively high catalytic activity (up to 2810 g mmol(**4**)$^{-1}$ h^{-1}).

Keywords: zirconium; oligomerization; polymerization

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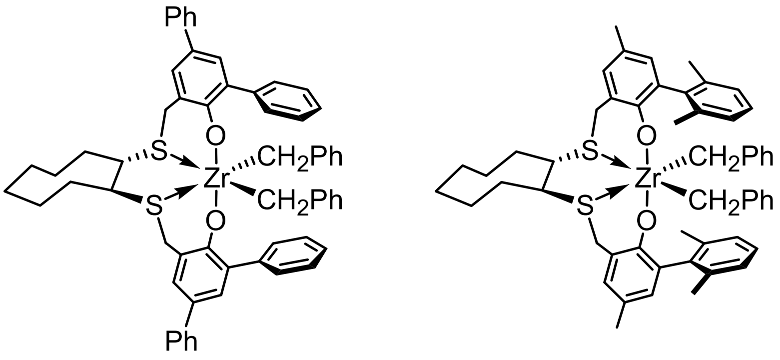
1. Introduction

Since the discovery of Ziegler-Natta catalyst and single-site metallocene catalyst, the development of precise oligomerization and polymerization catalysts for α-olefins has been attractive in both academic and industrial fields [1–4]. During the past two decades, considerable attention has been focused particularly on the development and design of early transition metal catalysts featuring non-Cp (cyclopentadienyl) ligands which demonstrate high activity and regio- and stereocontrols in the α-olefin polymerization [5–8]. Among them, dianionic [OSSO]-type tetradentate ligands, based on two phenoxide frameworks with two sulfur donors at the ortho- or benzyl-positions have been of great interest so far [9–37]. We have reported several Group 4 and 5 metal complexes having an original [OSSO]-type bis(phenolate) ligand possessing a *trans*-1,2-cyclooctanediyl platform [38–45]. The combination of these complexes and activators could achieve the controlled isotactic polymerization of various α-olefins involving excellent activity. Recently, we have also preliminarily investigated the preparation of dibenzyl zirconium(IV) complexes (**1** and **2**) bearing [OSSO]-type bis(phenolate) ligands substituted with phenyl or 2,6-dimethylphenyl (Dmp) groups on the phenolate groups (Scheme 1) [46]. Upon activation with dMAO (dried methylaluminoxane), the dibenzyl complexes **1** and **2** promote high performance in the polymerization of styrene (activity < 7700 g mmol(cat.)$^{-1}$ h^{-1}) yielding the corresponding isotactic polymers with molecular weights of M_w < 181,000 g $mmol^{-1}$. Moreover, these catalyst systems could catalyze the oligomerization of 1-hexene at low catalyst loadings (0.0019–0.0056 mol %) to yield the corresponding vinylidene-ended dimer (74–91%) as the main product with relatively high turnover frequencies (TOFs) up to 11,100 h^{-1} [47]. These successful results with aryl-substituted [OSSO]-type zirconium(IV) complexes stimulated us to expand further exploring the synthesis and catalytic performance of new [OSSO]-type complex in the oligomerization and polymerization of α-olefins. Herein we wish to present the synthesis of dibenzyl zirconium(IV) complex (**4**) incorporating with a carbazolyl(Cbz)-substituted [OSSO]-type preligand (**3**) and its performance in the oligomerization of 1-hexene together with polymerization of styrene, as a part of our investigation in the single-site non-Cp catalysis.

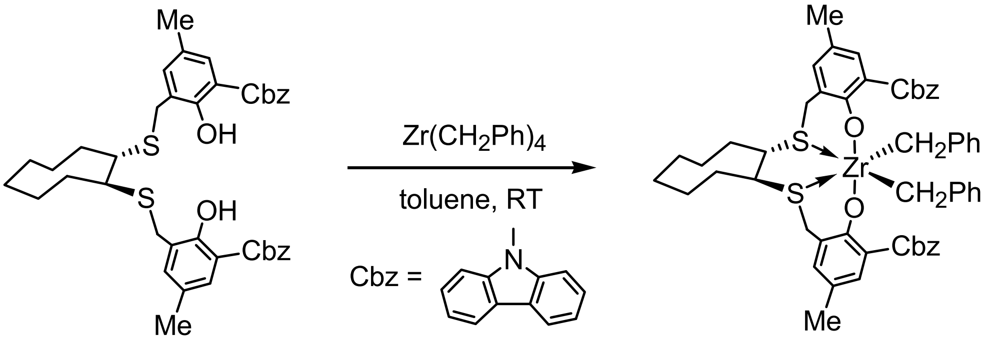


1 **2**

Scheme 1. Dibenzyl zirconium (IV) complexes **1** and **2** having [OSSO]-type bis(phenolate) ligands substituted with aryl groups.

2. Results and Discussion

A Cbz-substituted [OSSO]-type preligand **3** was prepared according to literature procedure [48], that is, by treatment of the corresponding 2-(bromomethyl)-6-(9*H*-carbazol-9-yl)-4-methylphenol and *trans*-cyclooctane-1,2-dithiol in the presence of Et_3N in Et_2O. The dibenzyl zirconium(IV) complex **4** was readily synthesized as pale yellow crystals in 93% yield by the reaction of **3** with $Zr(CH_2Ph)_4$ in toluene at room temperature (Scheme 2). In the ^1H NMR spectrum of **4**, an AB pattern for the *S*-benzyl geminal protons was observed at δ 2.82 and 2.99 as doublets with a coupling constant of 12 Hz. Two doublet signals for benzyl ligands appeared at considerably upfield (δ −0.05 and 0.88) with a coupling constant of 8 Hz, due to the shielding effect of aromatic rings in the Cbz groups. These observations indicate its C_2-symmetric structure in solution on the NMR time scale.

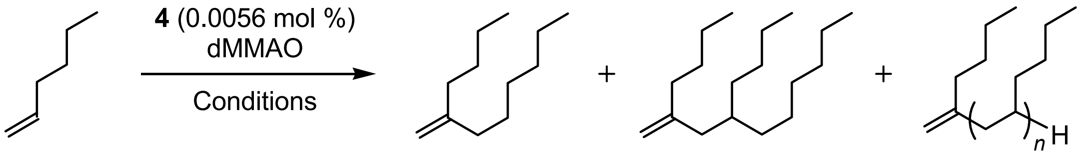


3 **4** (93%)

Scheme 2. Preparation of dibenzyl zirconium (IV) complex **4** with carbazolyl-substituted [OSSO]-type bis(phenolate) ligands.

To assess the polymerization ability of dibenzyl zirconium(IV) complex **4**, we examined the oligomerization of 1-hexene under various reaction conditions. The results are collected in Table 1. Upon activation with dMMAO (0.20 mmol), complex **4** (0.002 mmol, 0.0056 mol %) acted as a precatalyst to oligomerize 1-hexene (3.0 g, 35.6 mmol) without any solvents to give vinylidene-terminated oligomers with a low product conversion of 6.3% in 1 h at 25 °C (Table 1, Run 1). The corresponding TOF value is 1130 h^{-1}, which is still higher than that of MAO-activated zirconocene (TOF = 296 h^{-1}) [49], but approximately one-tenth reduced compared to that of phenyl-substituted [OSSO]-type complex **1** (TOF = 11,100 h^{-1}) [47]. This result would be explained by steric hindrance of bulky Cbz groups and reduced Lewis acidity of the active center by the electron donating Cbz groups. The microstructure of the resulting oligomers was estimated by ^{1}H and ^{13}C NMR spectroscopy. High 1,2-regioselectivity was confirmed in the ^{1}H NMR spectrum of the oligomers; the vinylidene selectivity was calculated to be 98% (see, Figure S2). The ^{13}C{^{1}H} NMR spectrum of the oligomers presented two sets for two vinylidene carbon atoms at 108.3 and 150.4 ppm as the major signals and approximately 110 and 150 ppm as minor signals corresponding to the dimer and other oligomers (including trimer) of 1-hexene, respectively (see, Figure S3). In contrast to precatalysts **1** and **2**, very weak resonances for vinylene-terminated groups were confirmed around 130 ppm. The relative integral ratio of these vinylidene signals suggested an oligomeric distribution as follow; 39% of dimer, 34% of trimer, and 27% of other oligomers. Increasing the amount of dMMAO to 150, 200, and 250 equivalents also resulted in the dominant production of vinylidene-ended oligomers including dimers of high contents in 56–62% (Table 1, Runs 2–4). The corresponding conversions and TOFs were recorded in the ranges of 7.6–9.5% and 1350–1690 h^{-1}, respectively, increasing with elevating the amount of dMMAO. In particular, it is noteworthy that 250 equivalents of dMMAO exhibited the highest TOF of 1690 h^{-1} in this study (Table 1, Run 4). When the reaction temperature was raised to 40 °C, a similar oligomerization proceeded successfully yielding vinylidene-terminated oligomers (Table 1, Run 5). The slightly increased conversion and TOF value were observed in 11.7% and 2080 h^{-1}, respectively. The obtained oligomers showed a dimer distribution of 53% similar to those in Runs 1–4. It is noteworthy that trimer distributions (21–34%) obtained with **4** are remarkably increased compared with those with precatalysts **1** and **2** (8–11%). Overall, the low conversions could be speculated by the decomposition of active species such as Zr−H intermediates during the reaction process.

Table 1. Oligomerization of 1-hexene using precatalyst **4** activated with dMMAO [a].

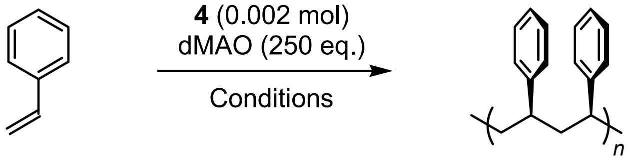


						Oligomer Distribution [c] [%]		
Run	**Al/Zr**	**Temp. [°C]**	**Conv. [%]**	**TOF [h^{-1}]**	**Vinylidene Selectivity [b] [%]**	**Dimer**	**Trimer**	**Others**
1	100	25	6.3	1130	98	39	34	27
2	150	25	7.6	1350	98	62	21	17
3	200	25	8.6	1540	98	56	25	18
4	250	25	9.5	1690	98	55	25	20
5	250	40	11.7	2080	98	53	26	21

[a] Conditions: **4** (0.002 mmol, 0.0056 mol %), 1-hexene (3.0 g, 35.6 mmol), reaction time: 1 h; [b] Estimated by ^{1}H NMR spectroscopy in $CDCl_3$; [c] Estimated by ^{13}C{^{1}H} NMR spectroscopy in $CDCl_3$.

Since dibenzyl zirconium(IV) complexes **1** and **2** featuring aryl-substituted [OSSO]-type ligands have already served as useful precatalysts for the isospecific polymerization of styrene [46], we next turned our attention to the polymerization of styrene employing Cbz-substituted precatalyst **4**. The results are summarized in Table 2. Similarly to the cases for complexes **1** and **2**, the polymerization of styrene (3.0 g, 28.8 mmol) using the system of **4** (0.002 mmol) and dMAO (0.5 mmol, 250 equiv.) in toluene at 0 °C occurred sluggishly to afford a crystalline polymer of 0.085 g, which corresponds to the activity of 85 g mmol(**4**)$^{-1}$ h^{-1} (Table 2, Run 6). An analysis with GPC revealed that the resulting polymer had a unimodal distribution with a quite large polydispersity index (PDI) of 20.3 and a large molecular weight M_w of 223,000 g mol^{-1}. The resulting large PDI value suggested that the reaction rate of the initiation process that gives the first initial active species from **4** is slower than that of the chain propagation process at low temperature. The $^{13}C\{^1H\}$ NMR spectrum of the obtained polymer exhibited six sharp peaks indicating the formation of an excellent isotactic polystyrene up to 99% of the [*mm*] triad (see, Figure S4). Since there is no observation of stereo irregular around the phenyl *ipso* carbon at 146.3 ppm [50], the detailed microstructure of the polystyrene is assigned to the [*mmmmmm*] heptad even with a very large PDI value. At 25 °C, the polymerization of styrene by **4**/dMAO system was somewhat accelerated to furnish 0.61 g of completely isotactic polystyrene ([*mm*] >99%) with the largest M_w of 508,000 g mol^{-1} in this study and still a large PDI of 4.2 (Table 2, Run 7). The corresponding activity of 414 g mmol(**4**)$^{-1}$ h^{-1} is increased compared to that at 0 °C. The production of isotactic polystyrene having a large M_w of 458,000 g mol^{-1} and a narrow PDI value of 2.8 was also found in the polymerization at 40 °C (Table 2, Run 8). These M_w are distinctly larger compared with those obtained with aryl-substituted precatalysts **1** and **2** (**1**: M_w = 9500–181,000 g mol^{-1}, **2**: M_w = 195,000–380,000 g mol^{-1}). The catalytic activity of 1000 g mmol(**4**)$^{-1}$ h^{-1} is approximately 2.4-folds higher than that at 25 °C. At 70 °C, **4**/dMAO system exhibited the highest activity of 2810 g mmol(**4**)$^{-1}$ h^{-1} (Table 2, Run 9), which is comparable to the related precatalysts for the isospecific polymerization of styrene at varied temperatures, [OSSO]-type titanium complex [330 g mmol^{-1} h^{-1} at 40 °C] [10] and yttrium and neodymium complexes supported by *ansa*-type Cp ligands [392–1637 g mmol^{-1} h^{-1} at 60–120 °C] [51], but remarkably lower than that of Dmp-substituted precatalyst **2** at the same temperature (7700 g mmol(**2**) $^{-1}$ h^{-1}). The low activity of **4** would be explained by the decrease of Lewis acidity of active species probably due to the substitution of the electron-donating Cbz group. Despite the high polymerization temperature, the yielding polystyrene is completely isotactic ([*mm*] >99%). Again, GPC analysis of the polystyrene showed a monomodal (M_w = 179,000 g mol^{-1}) and a PDI of around 2, indicating single-site polymerization behavior of **4**/dMAO system

Table 2. Polymerization of styrene using precatalyst **4** activated with dMAO [a].



Run	Temp. [°C]	Yield [g]	Activity [g mmol^{-1} h^{-1}]	M_w [g mol^{-1}]	PDI [b]	[*mm*] [c] [%]
6	0	0.085	85	223,000	20.3	>99
7	25	0.414	414	508,000	4.2	>99
8	40	1.00	1000	458,000	2.8	>99
9	70	2.81	2810	179,000	2.1	>99

[a] Conditions: **4** (0.002 mmol), [dMAO]/[4] = 250, styrene (3.0 g, 28.8 mmol), toluene 5 mL, reaction time: 30 min; [b] PDI (polydispersity index) = M_w/M_n, determined by GPC (PS standard); [c] Determined by $^{13}C\{^1H\}$ NMR spectroscopy in $CDCl_3$.

3. Materials and Methods

3.1. General

All air- and/or moisture-sensitive compounds were manipulated under an inert atmosphere of argon either using standard Schlenk-line techniques or in Glovebox Japan E300 gloveboxes (Tokyo, Japan). Toluene and hexane were purchased from Kanto Chemical (Tokyo, Japan) and were dried over a potassium mirror prior to use. 1-Hexene and styrene were purchased from Tokyo Chemical Industry (Tokyo, Japan) and dried over a potassium mirror for 1 h under argon atmosphere, and then degassed by the freeze-thaw cycle prior to use. C_6D_6 was dried over a potassium mirror for 1 h under argon atmosphere and was degassed by the freeze-thaw cycle prior to use. ^{1}H (400 MHz) and ^{13}C NMR (101 MHz) spectra were measured in $CDCl_3$ or C_6D_6 using a Bruker DPX-400 spectrometer (MA, USA). All melting points were determined on a Mel-Temp capillary tube apparatus (Saitama, Japan) and are uncorrected. The weight average molecular weights (M_w) and molecular weight distributions (M_w/M_n) of the polymers were determined at ambient temperature using a GPC KF-804L (Shodex Corporation, Tokyo, Japan) gel permeation chromatograph (GPC) equipped with a SCL-10AVP/LC-10ATVP/DGU-14A/CTO-10ACVP/RID-10A apparatus (Shimadzu Corporation, Kyoto, Japan). THF [purchased from Kanto Chemical (Tokyo, Japan)] was used as carrier solvent. The calibration curve was established with polystyrene standards as the reference. 2-(Bromomethyl)-6-(9*H*-carbazol-9-yl)-4-methylphenol [48], dMMAO [52], and dMAO [53] were prepared by the literature procedures.

3.2. Synthesis of Dibenzyl Zirconium(IV) Complex 4

A solution of $Zr(CH_2Ph)_4$ [54] (95 mg, 0.209 mmol) in toluene (2 mL) was added to a solution of **3** (157 mg, 0.209 mmol) in toluene (2 mL) at room temperature. The mixture was stirred for 17 h at room temperature, and the solvent was evaporated under reduced pressure. The resulting residue was rinsed with hexane and dried under reduced pressure to give dibenzyl zirconium(IV) complex **4** (198 mg) in 93% yield as pale yellow crystals. **4**: Mp 288–289 °C (dec.).

^{1}H NMR (400 MHz) δ –0.05 (d, *J* = 8 Hz, 2H, $ZrCH_2$), 0.88 (d, *J* = 8 Hz, 2H, $ZrCH_2$), 0.90–1.60 (m, 12H, CH_2), 1.96 (s, 6H, CH_3), 2.38 (s, 2H, CH), 2.82 (d, *J* = 12 Hz, 2H, SCH_2), 2.99 (d, *J* = 12 Hz, 2H, SCH_2), 5.63 (d, *J* = 8 Hz, 2H, Ar), 6.35 (s, 2H, Ar), 6.68 (t, *J* = 8 Hz, 2H, Ar), 6.75–6.81 (m, 6H, Ar), 7.00–7.02 (m, 2H, Ar), 7.08 (d, *J* = 8 Hz, 2H, Ar), 7.21–7.25 (m, 2H, Ar), 7.31–7.36 (m, 6H, Ar), 7.55 (t, *J* = 8 Hz, 2H, Ar), 8.04 (d, *J* = 8 Hz, 2H), 8.11 (d, *J* = 8 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz) δ 19.9 (CH_3), 25.2 (CH_2), 25.9 (CH_2), 28.6 (CH_2), 33.6 (SCH_2), 48.0 (CH), 57.6 (CH_2), 109.9 (CH), 110.4 (CH), 119.1 (CH), 120.6 (CH), 120.8 (CH), 122.5 (CH), 123.2 (C), 123.4 (C), 123.7 (C), 125.26 (CH), 125.31 (C), 125.7 (CH), 125.9 (C), 128.7 (CH), 129.0 (CH), 129.4 (CH), 130.3 (CH), 131.1 (CH), 141.66 (C), 141.71 (C), 143.0 (C), 155.4 (C).

3.3. General Procedure of 1-Hexene Oligomerization

To a 50 mL Schlenk-flask was charged sequentially **4** (0.0020 mmol, 0.0056 mol %) and dMMAO at 25 °C or 40 °C. After stirring 5 min at the temperature, 1-hexene (3.0 g, 35.6 mmol) was added to the reaction mixture. The reaction mixture was stirred for desired time at the temperature, and then MeOH and aqueous HCl were added to quench the reaction. Volatile materials were evaporated under reduced pressure, and the residue was extracted with CH_2Cl_2. The extract was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give oligo(1-hexene) as a colorless liquid.

3.4. General Procedure for Styrene Polymerization

To a 50 mL Schlenk-flask was charged sequentially **4** (0.0020 mmol), dMAO (0.50 mmol), and toluene (5 mL) at 25 °C. The reaction mixture was stirred for 5 min at the temperature, and then styrene (3.0 g, 28.8 mmol) was injected to the reaction mixture. After stirring for desired time at the temperature, the reaction was stopped by addition of MeOH and aqueous HCl, and volatile materials were removed under reduced pressure. The residue was extracted with CH_2Cl_2, and the extract was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure at 70 °C overnight to leave polystyrene.

4. Conclusions

We synthesized the dibenzyl zirconium(IV) complex **4** possessing a carbazolyl-substituted [OSSO]-type bis(phenolate) ligand as a new single-site non-Cp precatalyst. Oligomerization of

1-hexene using the combination of precatalyst **4** at relatively low catalyst loadings and dMMAO as an activator produced the corresponding vinylidene-terminated oligomers with moderate TOFs up to 2080 h^{-1}. The ^{13}C NMR analysis revealed that the resulting oligomers contained the dimer of 1-hexene as the main product in 39–62% distributions. Upon activation with dMAO, the precatalyst **4** promoted the polymerization of styrene to afford isotactic polystyrenes ([*mm*] > 99%) with quite large molecular weights M_w (508,100 g mol^{-1}) and relatively high catalytic activities up to 2810 g $mmol(\mathbf{4})^{-1}$ h^{-1}.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/6/528/s1, Figure S1: ^{1}H NMR spectrum of dibenzyl zirconium(IV) complex **4**, Figure S2: ^{1}H NMR spectrum of oligo(1-hexene) obtained by the **4**/dMMAO system at 25 °C (Table 1, Run 4), Figure S3: ^{13}C{^{1}H} NMR spectrum of oligo(1-hexene) obtained by the **4**/dMMAO system at 25 °C (Table 1, Run 4), Figure S4: ^{13}C{^{1}H} NMR spectrum of isotactic polystyrene obtained by the **4**/dMAO system at 70 °C (Table 2, Run 9).

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Conflicts of Interest: The authors declare no conflict of interest.

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