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

Norio Nakata *©, Kazuaki Nakamura, Shotaro Nagaoka and Akihiko Ishii *

Department of Chemistry, Graduate School of Science and Engineering, Saitama University, 255 Shimo-okubo, Sakura-ku, Saitama 338-8570, Japan; kazu21.mh.mc@gmail.com (K.N.); s.nagaoka.368@ms.saitama-u.ac.jp (S.N.)

* Correspondence: nakata@chem.saitama-u.ac.jp (N.N.); ishiiaki@chem.saitama-u.ac.jp (A.I.);
   Tel.: +81-48-858-3392 (N.N.); Fax: +81-48-858-3700 (N.N.)

Received: 9 May 2019; Accepted: 7 June 2019; Published: 13 June 2019

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 13C NMR analysis of the resulting oligomers revealed the formation of dimer-enriched oligo(1-hexene) 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

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.

![Scheme 1](image1.png)

**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-(9H-carbazol-9-yl)-4-methylphenol and trans-cyclooctane-1,2-dithiol in the presence of Et₃N in Et₂O. The dibenzyl zirconium(IV) complex 4 was readily synthesized as pale yellow crystals in 93% yield by the reaction of 3 with Zr(CH₂Ph)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 C₂-symmetric structure in solution on the NMR time scale.

![Scheme 2](image2.png)

**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 pre catalyst 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.

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

| Run | Al/Zr | Temp. [°C] | Conv. [%] | TOF [h\(^{-1}\)] | Vinylidene Selectivity [%] | 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\(_3\).
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 that than of the chain propagation process at low temperature. The \(^{13}\)C{\[^1\text{H}\]} NMR spectrum of the obtained polymer exhibited six sharp peaks indicating the formation of an excellent isotactic polystyrene up to 99\% of the \([mmm]\) 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 \([mmmmaaa]\) 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 \((\text{[mmm]} >99\%)\) 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: \( M_w = 9500–181,000 \text{ g mol}^{-1}\), 2: \( M_w = 195,000–380,000 \text{ g mol}^{-1}\)). 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, \([\text{OSSO}]-\text{type titanium complex} [330 \text{ g mmol}^{-1}\) h\(^{-1}\) at 40 °C] [10] and yttrium and neodymium complexes supported by \(\text{ansa}\)-type C\(_p\) ligands \([392–1637 \text{ g mmol}^{-1}\) h\(^{-1}\) at 60–120 °C] [51], but remarkably lower than that of Dmp-substituted precatalyst 2 at the same temperature \((7700 \text{ g mmol(2)}^{-1}\) 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 \((\text{[mmm]} >99\%)\). Again, GPC analysis of the polystyrene showed a monomodal \((M_w = 179,000 \text{ g mol}^{-1})\) 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.

| Run | Temp. [°C] | Yield [g] | Activity [g mmol\(^{-1}\) h\(^{-1}\)] | \( M_w \) [g mol\(^{-1}\)] | PDI \(^b\) | \[mmm\] \(^c\) [%] |
|-----|------------|-----------|------------------------------------|-----------------|----------------|----------------|
| 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{\[^1\text{H}\]} 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_{6}D_{6} was dried over a potassium mirror for 1 h under argon atmosphere and was degassed by the freeze-thaw cycle prior to use. 

\textsuperscript{1}H (400 MHz) and \textsuperscript{13}C NMR (101 MHz) spectra were measured in CDCl_{3} or C_{6}D_{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 (\textit{M}_{w}) and molecular weight distributions (\textit{M}_{w}/\textit{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\textit{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\textsubscript{2}Ph)\textsubscript{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. 

\textit{Mp} 288–289 °C (dec.).

\textit{1}H NMR (400 MHz) \(\delta\) -0.05 (d, \(J = 8\) Hz, 2H, ZrCH\textsubscript{2}), 0.88 (d, \(J = 8\) Hz, 2H, ZrCH\textsubscript{2}), 0.90–1.60 (m, 12H, CH\textsubscript{2}), 1.96 (s, 6H, CH\textsubscript{3}), 2.38 (s, 2H, CH), 2.82 (d, \(J = 12\) Hz, 2H, SCH\textsubscript{2}), 2.99 (d, \(J = 12\) Hz, 2H, SCH\textsubscript{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). \textit{13}C\textsuperscript{[\textit{1}\textit{H}]} NMR (101 MHz) \(\delta\) 19.9 (CH\textsubscript{3}), 25.2 (CH\textsubscript{2}), 25.9 (CH\textsubscript{2}), 28.6 (CH\textsubscript{2}), 33.6 (SCH\textsubscript{2}), 48.0 (CH), 57.6 (CH\textsubscript{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\textsubscript{2}Cl\textsubscript{2}. The extract was washed with water and dried over anhydrous Na\textsubscript{2}SO\textsubscript{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\textsubscript{2}Cl\textsubscript{2}, and the extract was washed with water and dried over anhydrous Na\textsubscript{2}SO\textsubscript{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 a fold isotactic polystyrenes ($[\text{mm}] > 99\%$) with quite large molecular weights $M_w$ (508,100 g mol$^{-1}$) and relatively high catalytic activities up to 2810 g mmol(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).

**Author Contributions:** Conceptualization, N.N. and A.I.; Funding acquisition, N.N.; Investigation, K.N. and S.N.; Data analysis, N.N., K.N., and S.N.; Project administration, N.N. and A.I.; Writing-original draft, N.N.; Writing-review and editing, N.N. and A.I.

**Funding:** This research received no external funding.

**Acknowledgments:** This work was supported by JSPS KAKENHI grants 25410035 and 17K05771. N.N. is also thankful for financial support from SEI Group CSR Foundation.

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

**References**

1. Resconi, L.; Chadwick, J.C.; Cavallo, L. Olefin polymerizations with group IV metal catalysts. In Comprehensive Organometallic Chemistry, 3rd ed.; Mingos, D.M.P., Crabtree, R.H., Eds.; Elsevier: Oxford, UK, 2016; Volume 4, pp. 1005–1166.
2. Fujita, T.; Makio, H. Polymerization of alkenes. In Comprehensive Organometallic Chemistry, 3rd ed.; Mingos, D.M.P., Crabtree, R.H., Eds.; Elsevier: Oxford, UK, 2016; Volume 11, pp. 691–734.
3. Baugh, L.S.; Canich, J.-A.M. Stereoselective Polymerization with Single-Site Catalysts; CRC Press: Boca Raton, FL, USA, 2008.
4. Osakada, K. Organometallics Reactions and Polymerization; Springer: Heidelberg, Germany, 2014.
5. Britovsek, G.J.P.; Gibson, V.C.; Wass, D.F. The search for new-generation olefin polymerization catalysts: Life beyond metallocenes. Angew. Chem. Int. Ed. 1999, 38, 428–447. [CrossRef]
6. Suzuki, Y.; Terao, H.; Fujita, T. Recent advances in phenoxy-based catalysts for olefin polymerization. Bull. Chem. Soc. Jpn. 2003, 76, 1493–1517. [CrossRef]
7. Givson, V.C.; Spitsmesser, S.K. Advances in non-metallocene olefin polymerization catalysis. Chem. Rev. 2003, 103, 283–316.
8. Givson, V.C.; Redshaw, C.; Solan, G.A. Bis(imino)pyridines: surprisingly reactive ligands and a gateway to new families of catalysts. Chem. Rev. 2007, 107, 1745–1776.
9. Nakata, N.; Toda, T.; Ishii, A. Recent advances in the chemistry of Group 4 metal complexes incorporating [OSSO]-type bis(pheno)lo) ligands as post-metallocene catalysts. Polym. Chem. 2011, 2, 1597–1610. [CrossRef]
10. Capacchione, C.; Proto, A.; Ebeling, H.; Mühlaupt, R.; Möller, K.; Spaniol, T.P.; Okuda, J. Ancillary ligand effect on single-site styrene polymerization: Isospecificity of group 4 metal bis(pheno)late catalysts. J. Am. Chem. Soc. 2003, 125, 4964–4965. [CrossRef] [PubMed]
11. Proto, A.; Capacchione, C.; Venditto, V.; Okuda, J. Synthesis of isotactic poly-1,2-(4-methyl-1,3-pentadiene) by a homogeneous titanium catalyst. Macromolecules 2003, 36, 9249–9251. [CrossRef]
12. Capacchione, C.; Proto, A.; Okuda, J. Synthesis of branched polyethylene by ethylene homopolymerization using titanium catalysts that contain a bridged bis(pheno)late ligand. J. Polym. Sci. Part A: Polym. Chem. 2004, 42, 2815–2822. [CrossRef]
13. Beckerle, K.; Capacchione, C.; Ebeling, H.; Manivannan, R.; Mühlaupt, R.; Proto, A.; Spaniol, T.P.; Okuda, J. Stereospecific post-metallocene polymerization catalysts: The example of isospecific styrene polymerization. J. Organomet. Chem. 2004, 689, 4636–4641. [CrossRef]
14. Capacchione, C.; De Carlo, F.; Zannoni, C.; Okuda, J.; Proto, A. Propylene–styrene multiblock copolymers: evidence for monomer enchainment via opposite insertion regiochemistry by a single-site catalyst. *Macromolecules* 2004, 37, 8918–8922. [CrossRef]

15. Capacchione, C.; Manivannan, R.; Barone, M.; Beckerle, K.; Centore, R.; Oliva, L.; Proto, A.; Tuzi, A.; Spaniol, T.P.; Okuda, J. Isospecific styrene polymerization by chiral titanium complexes that contain a tetradsentate [OSSO]-type bis(phenolato) ligand. *Organometallics* 2005, 24, 2971–2982. [CrossRef]

16. Beckerle, K.; Manivannan, R.; Spaniol, T.P.; Okuda, J. Living isospecific styrene polymerization by chiral benzyl titanium complexes that contain a tetradsentate [OSSO]-type bis(phenolato) ligand. *Organometallics* 2006, 25, 3019–3026. [CrossRef]

17. Lian, B.; Beckerle, K.; Spaniol, T.P.; Okuda, J. Stereospecific styrene enchainment at a titanium site within a helical ligand framework: Evidence for the formation of homochiral polystyrene. *Angew. Chem. Int. Ed.* 2006, 46, 8507–8510. [CrossRef] [PubMed]

18. Cohen, A.; Yeori, A.; Goldberg, I.; Kol, M. Group 4 complexes of a new [OSSO]-type dianionic ligand. Coordination chemistry and preliminary polymerization catalysis studies. *Inorg. Chem.* 2007, 46, 8114–8116. [CrossRef] [PubMed]

19. Okuda, S.; Cuomo, C.; Capacchione, C.; Zannoni, C.; Grassi, A.; Proto, A. Stereoselective polymerization of conjugated dienes and styrene–butadiene copolymerization promoted by octahedral titanium catalyst. *Macromolecules* 2007, 40, 5638–5643.

20. Capacchione, C.; Avagliano, A.; Proto, A. Ethylene–butadiene copolymerization promoted by titanium complex containing a tetradentate [OSSO]-type bis(phenolato) ligand. *Macromolecules* 2008, 41, 4573–4575. [CrossRef]

21. Gall, B.; Pelascini, F.; Ebeling, H.; Beckerle, K.; Okuda, J.; Mühlaupt, R. Molecular weight and end group control of isotactic polystyrene using olefins and nonconjugated diolefins as chain transfer agents. *Macromolecules* 2008, 41, 1627–1633. [CrossRef]

22. Proto, A.; Avagliano, A.; Saviello, D.; Capacchione, C. Copolymerization of ethylene with 4-methyl-1,3-pentadiene promoted by titanium complexes containing a tetradsentate [OSSO]-type bis(phenolato) ligand. *Macromolecules* 2009, 42, 6981–6985. [CrossRef]

23. Sergeeva, E.; Kopilov, J.; Goldberg, I.; Kol, M. Dithiodiolate ligands: Group 4 complexes and application in lactide polymerization. *Inorg. Chem.* 2010, 49, 3977–3979. [CrossRef]

24. Proto, A.; Avagliano, A.; Saviello, D.; Ricciardi, R.; Capacchione, C. Living, isoselective polymerization of styrene and formation of stereoregular block copolymers via sequential monomer addition. *Macromolecules* 2010, 43, 5919–5921. [CrossRef]

25. Capacchione, C.; Saviello, D.; Avagliano, A.; Proto, A. Copolymerization of ethylene with isoprene promoted by titanium complexes containing a tetradsentate [OSSO]-type bis(phenolato) ligand. *J. Polym. Sci. Part A: Polym. Chem.* 2010, 48, 4200–4206. [CrossRef]

26. Galdi, N.; Santoro, O.; Oliva, L.; Proto, A.; Capacchione, C. Asymmetric dihydrodimerization of styrene by a chiral zirconium complex containing a tetradsentate [OSSO]-type bis(phenolato) ligand. *Catal. Commun.* 2011, 12, 1113–1117. [CrossRef]

27. Konkol, M.; Nabika, M.; Kohno, T.; Hino, T.; Miyatake, T. Synthesis, structure, and α-olefin polymerization activity of group 4 metal complexes with [OSSO]-type bis(phenolate) ligands. *J. Organomet. Chem.* 2011, 696, 1792–1802. [CrossRef]

28. Ishii, A.; Asajima, K.; Toda, T.; Nakata, N. Synthesis of titanium(IV) and zirconium(IV) complexes with an [OSSO]-type bis(phenolate) ligand bearing a trans-cyclohexane-1,2-diyl ring and 1-hexene polymerization. *Organometallics* 2011, 30, 2947–2956. [CrossRef]

29. Cohen, A.; Goldberg, I.; Venditto, V.; Kol, M. Oscillating non-metallocenes - from stereoblock-isotactic polypropylene to isotactic polypropylene via zirconium and hafnium dithiodiphenolate catalysts. *Eur. J. Inorg. Chem.* 2011, 5219–5223. [CrossRef]

30. Capacchione, C.; Saviello, D.; Ricciardi, R.; Proto, A. Living, isoselective polymerization of 4-methyl-1,3-pentadiene and styrenic monomers and synthesis of highly stereoregular block copolymers via sequential monomer addition. *Macromolecules* 2011, 44, 7940–7947. [CrossRef]

31. Hu, P.; Wang, J.Q.; Wang, F.; Jin, G.X. Preparation, structure, and ethylene (co)polymerization behavior of group IV metal complexes with an [OSSO]-carborane ligand. *Chem. Eur. J.* 2011, 17, 8576–8583. [CrossRef] [PubMed]
References:

32. Costabile, C.; Capacchione, C.; Proto, A. Mechanistic studies on conjugated diene polymerizations promoted by a titanium complex containing a tetradeinate [OSSO]-type bis(phenolate) ligand. *Macromolecules* 2012, 45, 6363–6370. [CrossRef]

33. Buonerba, A.; Fienga, M.; Milione, S.; Cuomo, C.; Grassi, A.; Proto, A.; Capacchione, C. Binary copolymerization of p-methylstyrene with butadiene and isoprene catalyzed by titanium compounds showing different stereoselectivity. *Macromolecules* 2013, 46, 8449–8457. [CrossRef]

34. Hohberger, C.; Spaniol, T.P.; Okuda, J. Living polymerization by bis(phenolate) zirconium catalysts: Synthesis of isotactic polystyrene-block-polybutadiene copolymers. *Macromol. Chem. Phys.* 2014, 215, 2001–2006. [CrossRef]

35. Lapenta, R.; Buonerba, A.; De Nisi, A.; Monari, M.; Grassi, A.; Milione, S.; Capacchione, C. Stereo rigid OSSO-type group 4 metal complexes in the ring-opening polymerization of rac-lactide. *Inorg. Chem. 2017, 56*, 3447–3458. [CrossRef] [PubMed]

36. Ishii, A.; Ikuma, K.; Nakata, N.; Nakamura, K.; Kuribayashi, H.; Takaoki, K. Zirconium and hafnium complexes with cycloheptane- or cyclononane-fused [OSSO]-type bis(phenolate) ligands: Synthesis, structure, and highly active 1-hexene polymerization and ring-size effects of fused cycloalkanes on the activity. *Organometallics* 2017, 36, 3954–3966. [CrossRef]

37. Lapenta, R.; Buonerba, A.; Luciano, E.; Della Monica, F.; De Nisi, A.; Monari, M.; Grassi, A.; Capacchione, C.; Milione, C. Phenylene-bridged OSSO-type titanium complexes in the polymerization of ethylene and propylene. *ACS Omega* 2018, 3, 11608–11616. [CrossRef]

38. Nakata, N.; Ishii, A. Precise polymerization of α-olefins using a mixed donor-type ligand containing oxygen and sulfur atoms. *Koubunshi Ronbunshu* 2015, 72, 285–294. [CrossRef]

39. Ishii, A.; Toda, T.; Nakata, N.; Nakamura, K.; Kuribayashi, H.; Takaoki, K. Zirconium complex of an [OSSO]-type diphenolate ligand bearing trans-1,2-cyclooctanediylbis(thio) core: Synthesis, structure, and isospecific 1-hexene polymerization. *J. Am. Chem. Soc.* 2009, 131, 13566–13567. [CrossRef] [PubMed]

40. Nakata, N.; Toda, T.; Ishii, A.; Matsuo, T. Titanium complexes supported by an [OSSO]-type bis(phenolate) ligand based on a trans-cyclooctanediyl platform: Synthesis, structures, and 1-hexene polymerization. *Inorg. Chem. 2012, 51*, 274–281. [CrossRef] [PubMed]

41. Toda, T.; Nakata, N.; Ishii, A.; Matsuo, T. Synthesis, structure, and 1-hexene polymerization catalytic ability of group 5 metal complexes incorporating an [OSSO]-type ligand. *ACS Catal.* 2013, 3, 1764–1767. [CrossRef]

42. Nakata, N.; Toda, T.; Matsuo, T.; Ishii, A. Controlled isospecific polymerization of α-olefins by hafnium complex incorporating with a trans-cyclooctanediyl-bridged [OSSO]-type bis(phenolate) ligand. *Macromolecules* 2013, 46, 6758–6764. [CrossRef]

43. Toda, T.; Nakata, N.; Matsuo, T.; Ishii, A. Extremely active α-olefin polymerization and copolymerization with ethylene catalyzed by a dMAO-activated zirconium(IV) dichloro complex having an [OSSO]-type ligand. *RSC Adv.* 2015, 5, 88826–88831. [CrossRef]

44. Saito, Y.; Nakata, N.; Ishii, A. Highly isospecific polymerization of silyl-protected ω-alkenols with an [OSSO]-type bis(phenolate) dichloro zirconium(IV) precatayst. *Macromol. Rapid Commun.* 2016, 37, 969–974. [CrossRef]

45. Nakata, N.; Watanabe, T.; Toda, T.; Ishii, A. Enantio- and stereoselective cyclopolymerization of hexa-1,5-diene catalyzed by zirconium complexes possessing optically active bis(phenolate) ligands. *Macromol. Rapid Commun.* 2016, 37, 1820–1824. [CrossRef] [PubMed]

46. Nakata, N.; Toda, T.; Saito, Y.; Watanabe, T.; Ishii, A. Highly active and isospecific styrene polymerization catalyzed by zirconium complexes bearing aryl-substituted [OSSO]-type bis(phenolate) ligands. *Polymers* 2016, 31, 8. [CrossRef] [PubMed]

47. Nakata, N.; Nakamura, K.; Ishii, A. Highly efficient and 1,2-regioselective method for the oligomerization of 1-hexene promoted by zirconium precatalysts with [OSSO]-type bis(phenolate) ligands. *Organometallics* 2018, 37, 2640–2644. [CrossRef]

48. Takano, M.; Ito, K.; Ishii, A.; Nakata, N.; Kawauchi, F. JP 2013166735. *Jpn. Kokai Tokkyo Koho 2013.*

49. Harvey, B.G.; Meylemans, H.A. 1-Hexene: A renewable C6 platform for full-performance jet and diesel fuels. *Green Chem.* 2014, 16, 770–776. [CrossRef]

50. Harwood, H.J.; Chen, T.K.; Lin, F.T. 75-MHz 13C NMR Studies on Polystyrene and Epimerized Isotactic Polystyrenes. *ACS Symp. Ser.* 1984, 247, 197–222.
51. Rodrigues, A.-S.; Kirillov, E.; Roisnel, T.; Razavi, A.; Vuillemin, B.; Carpentier, J.-F. Highly isospecific styrene polymerization catalyzed by single-component bridged bis(indenyl) allyl yttrium and neodymium complexes. *Angew. Chem. Int. Ed.* 2007, 46, 7240–7243. [CrossRef] [PubMed]

52. Tanaka, R.; Kawahara, T.; Shinto, Y.; Nakayama, Y.; Shiono, T. An alternative method for the preparation of trialkylaluminum-depleted modified methylaluminoxane (dMMAO). *Macromolecules* 2017, 50, 5989–5993. [CrossRef]

53. Hasan, T.; Ioku, A.; Nishii, K.; Shiono, T.; Ikeda, T. Syndiospecific living polymerization of propene with [t-BuNSiMe2Flu]TiMe2 using MAO as cocatalyst. *Macromolecules* 2001, 34, 3142–3145. [CrossRef]

54. Rong, Y.; Al-Harbi, A.; Parkin, G. Highly variable Zr-CH2-Ph bond angles in tetrabenzylzirconium: Analysis of benzyl ligand coordination modes. *Organometallics* 2012, 31, 8208–8217. [CrossRef]