

# Synthesis of Aryloxo-Modified Half-Titanocenes as Highly Active Ethylene (Co)polymerization Catalysts: Notable Effect of Aryloxo *para*-Substituent

Suphitchaya Kitphaitun,<sup>a</sup> Qing Yan,<sup>a</sup> Konstantin Preradović,<sup>a</sup> Ken Tsutsumi,<sup>a</sup>  
and Kotohiro Nomura<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

\*Corresponding author: +81-42-677-2547, ktnomura@tmu.ac.jp

**Abstract:** Ethylene polymerization using a series of *nonbridged* half-titanocenes, Cp\*TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>-4-X-C<sub>6</sub>H<sub>2</sub>) [X = H, *t*Bu, Ph, 4-*t*BuC<sub>6</sub>H<sub>4</sub>, Ph<sub>2</sub>CH, Ph<sub>3</sub>C, 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, SiMe<sub>3</sub>, SiEt<sub>3</sub>], have been explored in the presence of MAO. Trialkylsilyl substituted (X = SiMe<sub>3</sub>, SiEt<sub>3</sub>) complexes exhibited the highest catalytic activities, and these complexes also showed the efficient comonomer incorporations similar to the reported one (X = H) in ethylene/2-methyl-1-pentene copolymerization.

**Keywords:** Olefin Polymerization, Titanium Complex Catalyst, Homogeneous Catalyst.

## 1. Introduction

Transition metal catalyzed olefin polymerization is a core technology for production of polyolefins that covers almost 50 % production of commercialized synthetic polymers in the world. In this research field, considerable attention has been paid recently to synthesis of new polymers that cannot be (or are very difficult to be) prepared by ordinary catalysts such as Ziegler-Natta, ordinary metallocene, linked-half metallocene (so called constrained geometry, CGC), and so called non-metallocene catalysts.<sup>1-3</sup> Half-titanocenes containing anionic donor ligands, Cp\*TiX<sub>2</sub>(Y) (Y = aryloxo, ketimide etc.), are promising candidates as the efficient catalysts due to their promising characteristics demonstrated especially in ethylene copolymerization (with  $\alpha$ -olefin, styrene, cyclic olefins, and sterically encumbered olefins).<sup>2,3</sup> It has been demonstrated that effective catalysts for the desired copolymerization can be tuned by the ligand modification (Cp', Y).<sup>2,3</sup> It has also been known that both Cp\* (C<sub>5</sub>Me<sub>5</sub>) and two isopropyl groups in the phenoxy ligand play a role for exhibiting the high activity in ethylene polymerization due to formation of unique structure [rather linear Ti-O-C(phenyl) bond angle] that leads to stabilization of the proposed active (cationic alkyl) species by O→Ti  $\pi$ -donation.<sup>3-6</sup> Therefore, in this paper, we wish to introduce our explored results concerning effect of *para*-substituent in the phenoxy ligand in Cp\*TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>-4-X-C<sub>6</sub>H<sub>2</sub>) (Chart 1) toward the catalytic activities in ethylene polymerization in the presence of methylaluminoxane (MAO) cocatalyst.

## 2. Experimental

All synthetic experiments were carried out under nitrogen atmosphere in a drybox. Ethylene (co)polymerizations were conducted in toluene in the presence of d-MAO prepared by removing toluene and AlMe<sub>3</sub> from the commercially available MAO (TMAO, Tosoh Finechem Co.). Molecular weights and molecular weight distributions for the resultant polymers were measured by GPC in *o*-dichlorobenzene at 140 °C, and their microstructural analysis was explored by <sup>13</sup>C NMR spectra.

## 3. Results and discussion

A series of aryloxo-modified half-titanocenes, Cp\*TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>-4-X-C<sub>6</sub>H<sub>2</sub>) [X = H (1), *t*Bu (2), Ph (3), 4-*t*BuC<sub>6</sub>H<sub>4</sub> (4), Ph<sub>2</sub>CH (5), Ph<sub>3</sub>C (6), 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (7), SiMe<sub>3</sub> (8), SiEt<sub>3</sub> (9), Chart 1] have been prepared

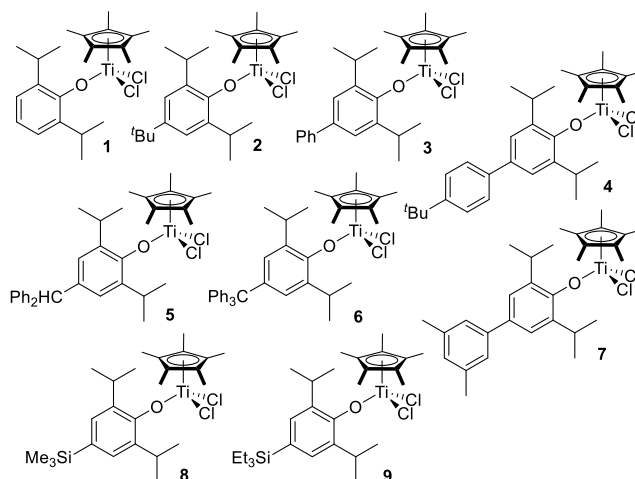


Chart 1. List of complexes employed in this study.

by analogous method for reported synthesis of **1**,<sup>4</sup> **2**,<sup>6</sup> by reaction of Cp\*TiCl<sub>3</sub> with corresponding lithium phenoxide in Et<sub>2</sub>O, and the resultant complexes (**3-9**) were identified by NMR spectra, elemental analysis and some structures were determined by X-ray crystallography (as exemplified in Figure 1 for complexes **8** and **9**).

As observed in complexes **1** and **2**,<sup>4,6</sup> these complexes (**8**, **9**) fold a distorted tetrahedral geometry around titanium. No significant differences in their bond distances and angles compared to **1** and **2** were observed, except that their Ti-O bond distances are rather long. These complexes also possess rather linear Ti-O-C(in phenyl) bond angles [172.5(3)°, 174.62(19)° for **8**, **9**, respectively], as observed in **1** and **2** [173.0(3)°, 173.0(3)° for **1**, **2**, respectively], indicating a presence of a rather strong O→Ti π-donation.

Table 1 summarizes results for ethylene polymerization in toluene using **1-9** in the presence of MAO cocatalyst. It turned out that the catalytic activity at 25 °C was affected by the *para* substituents, and the activity increased in the order: X = Ph<sub>3</sub>C (**6**) < Ph<sub>2</sub>CH (**5**), 4-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub> (**4**) < H (**1**) < C<sub>6</sub>H<sub>5</sub> (**3**) < 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**7**), SiMe<sub>3</sub> (**8**) < SiEt<sub>3</sub> (**9**). In particular, complex **9** showed the highest activity under the same conditions. Note that the activity by **9** increased at high temperature, whereas decrease in the activity by **1** was observed at 60 °C; the high activity by **9** (116000 kg-PE/mol-Ti·h) was maintained even at 80 °C.

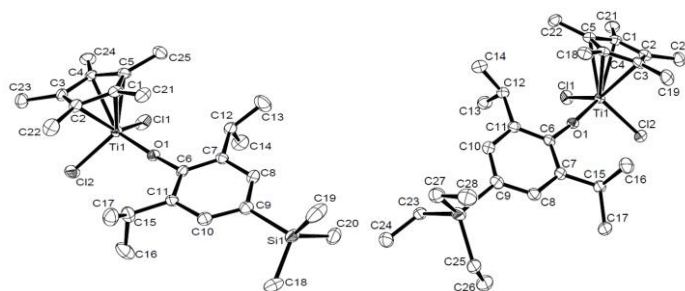
It should also be noted that these catalysts, especially **8** and **9** showed efficient comonomer incorporation in ethylene/2-methyl-1-pentene copolymerization similar to that by **1**;<sup>7</sup> the activities by **8** and **9** were higher than that by **1** conducted under the same conditions. The results clearly indicate that these catalysts (**8,9**) are promising highly active catalysts for efficient ethylene copolymerization. More details will be introduced in the conference.

#### 4. Conclusions

A series of *nonbridged* half-titanocenes, Cp\*TiCl<sub>2</sub>(O-2,6-<sup>i</sup>Pr<sub>2</sub>-4-X-C<sub>6</sub>H<sub>2</sub>) [X = H (**1**), <sup>t</sup>Bu (**2**), Ph (**3**), 4-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub> (**4**), Ph<sub>2</sub>CH (**5**), Ph<sub>3</sub>C (**6**), 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**7**), SiMe<sub>3</sub> (**8**), SiEt<sub>3</sub> (**9**)] have been prepared and identified. Trialkylsilyl substituted complexes (**8** and **9**) showed higher catalytic activities than the reported catalyst **1**, and these complexes also showed the similar efficient comonomer incorporations with higher catalytic activities in ethylene/2-methyl-1-pentene copolymerization.

#### References

1. K. Osakada (Ed.), *Organometallic Reactions and Polymerization*, Springer-Verlag: Berlin, 2014.
2. K. Nomura, *Dalton Trans.*, 8811 (2009).
3. K. Nomura, J. Liu, *Dalton Trans.*, 40 (2011) 7666.
4. K. Nomura, N. Naga, M. Miki, K. Yanagi, A. Imai, *Organometallics*, 17 (1998) 2152.
5. K. Nomura, A. Fudo, *Inorg. Chim. Acta* 345 (2003) 37.
6. K. Nomura, A. Tanaka, S. Katao, *J. Mol. Catal. A: Chem.* 254 (2006) 197.
7. K. Nomura, K. Itagaki, M. Fujiki, *Macromolecules*, 38 (2005) 2053.



**Figure 1.** ORTEP drawings for Cp\*TiCl<sub>2</sub>(O-2,6-<sup>i</sup>Pr<sub>2</sub>-4-SiMe<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>) (**8**, left), Cp\*TiCl<sub>2</sub>(O-2,6-<sup>i</sup>Pr<sub>2</sub>-4-SiEt<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>) (**9**, right).

**Table 1.** Ethylene polymerization by Cp\*TiCl<sub>2</sub>(O-2,6-<sup>i</sup>Pr<sub>2</sub>-4-X-C<sub>6</sub>H<sub>2</sub>) – MAO catalysts (ethylene 4 atm, toluene).<sup>a</sup>

Cp*TiCl <sub>2</sub> (O-2,6- <sup>i</sup> Pr <sub>2</sub> -4-XC <sub>6</sub> H <sub>2</sub> ) X	/ μmol	temp. / °C	activity kg-PE/mol-Ti·h
H ( <b>1</b> )	0.015	25	48100
H ( <b>1</b> ) <sup>b</sup>	0.010	25	53400
H ( <b>1</b> ) <sup>b</sup>	0.010	60	29400
<sup>t</sup> Bu ( <b>2</b> )	0.015	25	53500
C <sub>6</sub> H <sub>5</sub> ( <b>3</b> )	0.015	25	50700
4- <sup>t</sup> BuC <sub>6</sub> H <sub>4</sub> ( <b>4</b> )	0.015	25	46700
Ph <sub>2</sub> CH ( <b>5</b> )	0.015	25	46500
Ph <sub>3</sub> C ( <b>6</b> )	0.015	25	36900
3,5-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ( <b>7</b> )	0.015	25	54600
SiMe <sub>3</sub> ( <b>8</b> )	0.015	25	54500
SiEt <sub>3</sub> ( <b>9</b> )	0.015	25	57200
SiEt <sub>3</sub> ( <b>9</b> )	0.005	60	82800
SiEt <sub>3</sub> ( <b>9</b> )	0.005	80	116000

<sup>a</sup>Conditions: toluene 30 mL, MAO 3.0 mmol, ethylene 4 atm, 10 min. <sup>b</sup>MAO 4.0 mmol.