New Bis(salicylaldiminato) Titanium Complexes for Ethylene Polymerization

Shigekazu Matsui, Yasushi Tohi, Makoto Mitani, Junji Saito, Haruyuki Makio,
Hidetsugu Tanaka,† Masatoshi Nitabaru, Takashi Nakano,† and Terunori Fujita*
Petrochemicals Laboratory, Mitsui Chemicals, Inc., Waki-cho, Kuga-gun, Yamaguchi 740-0061
†*Computational Science Department, Mitsui Chemicals, Inc., Waki-cho, Kuga-gun, Yamaguchi 740-0061*

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New bis(salicylaldiminato) titanium complexes were synthesized and investigated as ethylene polymerization catalysts. These complexes, when activated with methylalumoxane, exhibited one of the highest activities displayed by group 4 transition metal complexes having no cyclopentadienyl ligand(s).

Research and development of transition metal complexes for olefin polymerization has made a dramatic impact on the polyolefin industry, as demonstrated by the discovery of group 4 metallocene catalyst systems.[1] Therefore, transition metal complexes having no cyclopentadienyl (Cp) ligand(s) have been intensively investigated in an attempt to create post-metallocene catalysts. However, little has been known about group 4 metal complexes with no Cp ligand(s) displaying high olefin polymerization activity though many complexes in this category have been investigated.[2-4]

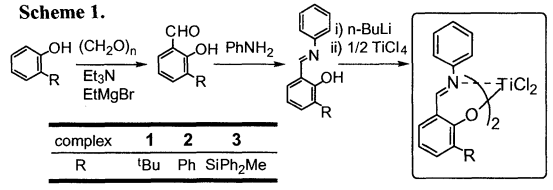
Alternatively, and recently, a number of late transition metal complexes having no Cp ligand(s) have been reported to display considerable olefin polymerization activity, for example, diimine nickel or palladium complexes,[5] iminopyridine iron or cobalt complexes,[6] and salicylaldimine nickel complexes.[7] Reported results show that Cp ligand(s) is not a must for olefin polymerization catalysts.

Considering the inherent properties of group 4 metals, we believe that group 4 metal complexes having no Cp ligand(s) also exhibit high olefin polymerization activity.

In this study,[8] we utilized a titanium complex having bidentate salicylaldimine chelate ligands. Transition metal complexes possessing bidentate salicylaldimine chelate ligand(s) have been well studied.[7,9,10] A recent example concerning olefin polymerization is the nickel complex reported by Grubbs, et al.[7] Nevertheless, few group 4 metal complexes possessing bidentate salicylaldimine ligand(s) have been reported as a polymerization catalyst, thus far.[9]

Here, therefore, we describe new bis(salicylaldiminato) titanium complexes displaying high ethylene polymerization activity. A general synthetic route for these complexes is summarized in Scheme 1.

Scheme 1.

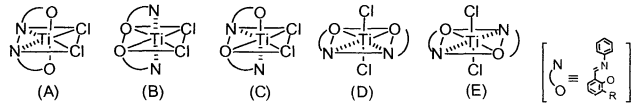


complex	1	2	3
R	^{t}Bu	Ph	$SiPh_2Me$

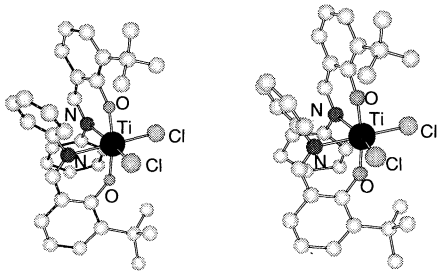
For example, complex **1**, bis[N-(3-t-butylsalicylidene)-phenylaminato]titanium(IV) dichloride, was prepared as follows: An ortho-formylation of 2-t-butylphenol with paraformaldehyde using Grignard reagent and triethylamine in toluene produced 3-t-butylsalicylaldehyde in 82% yield.[11] This aldehyde easily reacted with aniline in ethanol to afford N-(3-t-butylsalicylidene)aniline in 95% yield.[12] Complexation was achieved by the usual manner, that is, a reaction of 2 equiv of N-(3-t-butylsalicylidene)aniline lithium salt with $TiCl_4$ in diethyl ether furnished complex **1** in 61% yield as a red brown powder.[13] Complexes **2** and **3** as indicated in Scheme 1 were also synthesized using the corresponding materials.[13]

Since complexes **1-3** possess five possible isomeric structures, (A)-(E), as depicted in Scheme 2 below, we ascertained what was the most stable isomeric structure by means of DFT calculation.[14] As a consequence, these complexes exist best as isomeric structure (A).

Scheme 2.



Calculated isomeric structure (A) for complex **1** (Figure 1-(a) below), was found to be in good accordance with its X-ray structure (Figure 1-(b)).[15] Meaning, two oxygen atoms are situated in trans-position, whilst two nitrogen atoms and two chlorine atoms are situated in cis-position in the structures of complex **1**.



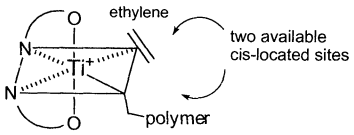
(a) DFT Calculation (b) X-ray analysis

Figure 1. Structures of complex **1**.

An active species of group 4 metal complexes for olefin polymerization is known to be an alkyl cationic complex, having two available cis-located sites needed for polymerization,[4] generated by the reaction of catalyst precursors, for example, a dichloro complex, with methylalumoxane (MAO). As two chlorine atoms, being situated in cis-position in a bis-(salicylaldiminato) titanium dichloride complex, are to be an alternative for a polymer-bonded site and an ethylene

coordinated site vis-a-vis polymerization, a structure of corresponding alkyl cationic complex should have two available cis-located sites needed for polymerization, as shown in Scheme 3.

Scheme 3.



Hence, complexes **1-3** were investigated as ethylene polymerization catalysts using MAO as a cocatalyst.[16] Polymerization results are summarized in Table 1.

Table 1. Ethylene polymerization results using complexes **1-3**/MAO

Entry	Cat.	Temp. /°C	Yield / g	Activity / kg-PE•mmol-Ti^{-1}•h^{-1}	Mv[17] / 10^4
1[a]	**1**	25	2.82	3.4	51.6
2[a]	**1**	50	3.30	4.0	54.6
3[a]	**1**	75	3.14	3.8	44.0
4[b]	**1**	25	1.38	3.3	51.0
5[b]	**2**	25	1.93	4.6	60.4
6[a]	**3**	25	2.05	2.5	37.5
7[c]	**1**	75	11.96	47.8	66.4

Conditions: MAO (Al); 1.25 mmol,
[a] Cat.; 5 μmol, reaction time; 10 min. in toluene (250 ml) under 0.1 MPa pressure,
[b] Cat.; 5 μmol, reaction time; 5 min. in toluene (250 ml) under 0.1 MPa pressure,
[c] Cat.; 1 μmol, reaction time; 15 min. in heptane (500 ml) under 0.9 MPa pressure.

Complex **1** exhibited an activity value of 3.4 kg-PE/mmol-Ti·h in toluene at 25 °C (Entry 1). This value is one of the highest values displayed by any group 4 metal complex with no Cp ligand(s).[2-4] The viscosity-average molecular weight (Mv) of the polymer obtained[17] was 51.6×10^4. Melting temperature (Tm) of the polymer obtained was 134.6 °C, showing a typical linear polyethylene, which is produced by general group 4 metal complexes.

Increasing polymerization temperature from 25 °C through 50 °C to 75 °C gave rise to no significant change vis-a-vis catalyst activity. Neither were there any significant changes regarding Mv values of the polymers (Entry 1,2,3). The observation concerning Mv values is noteworthy since, normally, an Mv value decreases with the increase in polymerization temperature. Molecular weight of polymers produced by Cp_2ZrCl_2 decreased dramatically with an increase in temperature.[18]

Complexes **2** and **3** also exhibited high polymerization properties. Thus, Complex **2** having a phenyl group at the R position furnished 4.6 kg-polymer/mmol-cat.·h of activity with an Mv of 60.4×10^4 (Entry 5). Complex **3** having a diphenylmethylsilyl group at the R position afforded 2.5 kg-PE/mmol-Ti·h of activity with an Mv of 37.5×10^4 (Entry 6). These results indicate that bis(salicylaldiminato) titanium complexes are potential ethylene polymerization catalysts.

Further, polymerization using complex **1** under 0.9 MPa ethylene pressure furnished very high activity, 47.8 kg-PE/mmol-Ti·h, and a high Mv value, 65.8×10^4 (Entry 7). This catalytic performance is enough for industrial production.

In conclusion, this study indicates that complexes **1-3** having two salicylaldimine ligands display high ethylene polymerization activity, suggesting that a Cp ligand is not a must for achieving high olefin polymerization activity. Further studies aiming at acquiring new olefin polymerization catalysts based on group 4 metal complexes having no Cp ligand(s) are now in progress.

References and Notes

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12 ^{1}H-NMR ($CDCl_3$); δ 1.47 (s, 9H), 6.8-7.5 (m, 8H), 8.67 (s, 1H), 13.95 (s,1H).

13 Complex **1**: ^{1}H-NMR ($CDCl_3$); δ 1.34, 1.35, 1.62, 6.75-7.32, 7.41-7.43, 7.55- 7.57, 7.62- 7.64, 7.92, 8.05, 8.07. Anal. Found; C, 64.98; H, 5.75; N, 4.44%. Calcd for $C_{34}H_{36}N_2O_2TiCl_2$; C, 65.50; H, 5.82; N, 4.49%. FD-mass, 622 (M+).
Complex **2**: ^{1}H-NMR ($CDCl_3$); δ 6.90-7.96, 8.00. Anal. Found; C, 68.61; H, 4.49; N, 4.14%. Calcd for $C_{38}H_{28}N_2O_2TiCl_2$; C, 68.80; H, 4.25; N, 4.22%. FD-mass, 662 (M+).
Complex **3**: ^{1}H-NMR ($CDCl_3$), δ 0.55-1.30, 7.51-7.81, 7.85, 7.90.
Anal. Found; C, 68.81; H, 5.25; N, 2.80%. Calcd for $C_{52}H_{44}N_2O_2Si_2TiCl_2$; C, 69.10; H, 4.91; N, 3.10%. FD-mass, 900 (M+).
(Complex **1-3** exists as isomeric mixtures in $CDCl_3$ solution.)

14 DFT calculation has been widely used for structural determination of transition metal complexes, c.f; L. Deng, T. Zieglar, T. K. Woo, P. Margl, and L. Fan, *Organometallics*, **17**, 3240 (1998).
All calculations were performed using gradient corrected density functional method BLYP, by means of the Amsterdam Density Functional (ADF) program. We used the triple -ζ basis set on the metal center, the double- ζ basis set on the Cl, N and O atoms, and the single-ζ basis set on the other atoms.

15 A single crystal was obtained from diethyl ether / pentane solution of complex **1**. Crystal data for complex **1**: Formula $TiC_{34}H_{36}O_2N_2Cl_2$, F.W. = 623.46, orthorhombic system, space group Pbca(#61), a = 17.064(6) Å, b = 26.395(6) Å, c = 15.986(7) Å, V= 7200(4) Å^3, Z = 8, D_{calc} = 1.143 g/cm^3, R = 0.158, Rw = 0.209, F_{000} = 2520.00, 8492 unique reflections (R_{int} = 0.314) were collected, λ (Mo-kα) = 4.10 cm^{-1}.

16 General polymerization procedure; Flow of ethylene gas (100 L/h) was charged into 250 ml of toluene at 25 °C. To this solution, MAO (Albemarle MAO, 1.2mmol/ml of a toluene solution) and a toluene solution of a complex was added at designated polymerization temperature. After the prescribed time, 25 ml of isobutanol was added to terminate the polymerization.

17 Mv values were calculated from the following equation, $[\eta]=6.2\times10^{-4}Mv^{0.7}$; R. Chiang, *J. Polymer Sci.*, **36**, 91 (1959).
Intrinsic viscosity [η] was measured in decalin at 135 °C using an Ubbelohde viscometer. The molecular weight distribution (Mw/Mn) value was ca. 2, determined by GPC measurement.

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