New Bis(salicylaldiminato) Titanium Complexes for Ethylene Polymerization

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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]

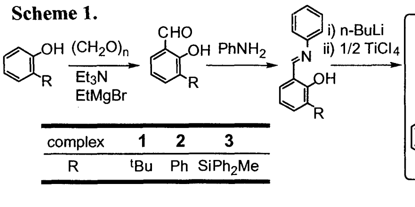
Alternatively, and recently, a number of late transition metal complexes having no Cp ligand(s) have been reported to display considerable olefin polymerization activity, for example, diimine nickel or palladium complexes,[5] iminopyridine iron or cobalt complexes,[6] and salicylaldimine nickel complexes.[7] 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.

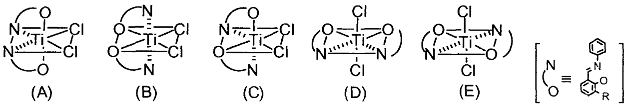


complex	1	2	3
R	^{t}Bu	Ph	$SiPh_2Me$

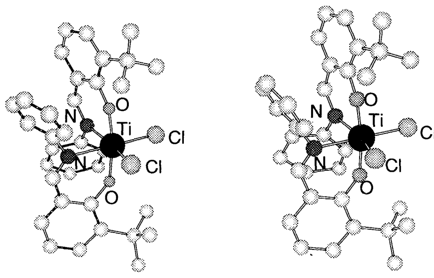
For example, complex **1**, bis[N-(3-t-butylsalicylidene)-phenylaminato]titanium(IV) dichloride, was prepared as follows: An ortho-formylation of 2-t-butylphenol with paraformaldehyde using Grignard reagent and triethylamine in toluene produced 3-t-butylsalicylaldehyde in 82% yield.[11] This aldehyde 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**.

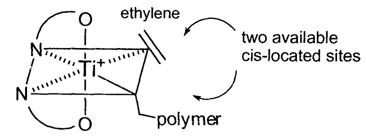


(a) DFT Calculation (b) X-ray analysis

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 ℃ (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 ℃, showing a typical linear polyethylene, which is produced by general group 4 metal complexes.

Increasing polymerization temperature from 25 ℃ through 50 ℃ to 75 ℃ 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-k*a*) = 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.
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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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