Post-Metallocenes: New Bis(pyrrolyl-2-aldiminato) Titanium Complexes for Ethylene Polymerization

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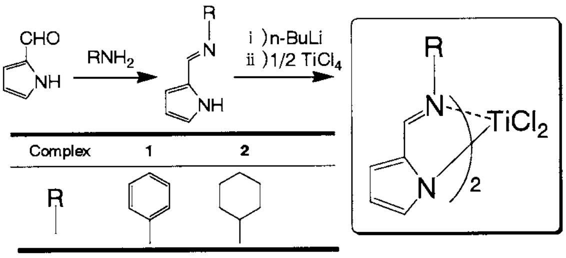
Two new bis(pyrrolyl-2-aldiminato) titanium complexes were synthesized and their structures determined by X-ray analyses. These complexes displayed high ethylene polymerization activity using MAO or $Ph_3C^+B^-(C_6F_5)_4/{}^iBu_3Al$ as a cocatalyst. One of the complexes exhibited very high ethylene polymerization activity (14100 kg-polymer·mol-Ti^{-1}·h^{-1}) with very high molecular weight (M_v: 260.1×10^4) using MAO as a cocatalyst.

After the sensational discovery[1] of highly active group 4 metallocene catalysts, much effort has been devoted to the research on well-defined transition metal complexes with a view to acquiring new olefin polymerization catalysts.[2] In consequence, a certain number of high performance olefin polymerization catalysts based on late transition metals have been developed.[3] However, till recently, other than group 4 metallocene catalysts, little has been known about group 4 transition metal complexes which display high catalytic performance for olefin polymerization. Very recently, we found zirconium complexes with two bidentate salicylaldimine ligands, which display exceptionally high ethylene polymerization activity, as a result of the study of group 4 transition metal complexes having multidentate and non-symmetric ligands.[4] Alternatively, a number of titanium complexes which possess intriguing catalytic properties for olefin polymerization have been reported.[5] There are, however, only a few examples of titanium complexes displaying high ethylene polymerization activity,[6] though titanium is a major player in highly active solid Ziegler–Natta catalysts. At this time, we have found highly active new titanium complexes possessing two pyrrolide-imine ligands,[7] they being multidentate and non-symmetric ligands.[8] Therefore, in this paper, we would like to describe these titanium complexes.

Scheme 1.



A general synthetic route for titanium complexes having two pyrrolide-imine ligands is shown in Scheme 1. For instance, complex **1** was prepared as follows: Reaction of pyrrole-2-carboxyaldehyde with aniline in dry EtOH using formic acid as a catalyst at rt for 72 h afforded *N*-(2-pyrrolidene)aniline in 65% yield. Treatment of 2 equiv of lithium salt of *N*-(2-pyrrolidene)aniline with $TiCl_4$ in dry diethyl ether furnished complex **1** in 79% yield as a black powder. Likewise, complex **2** was synthesized in a similar manner.

As a result of X-ray analyses, complexes **1** and **2** were revealed to have a similar stereochemical structure (complex **1**: Figure 1).[9] That is to say, they adopted a distorted octahedral structure around the titanium center. A pyrrole group is attached to the titanium metal by virtue of not π-bonding but σ-bonding. Two pyrrole-nitrogen atoms were situated in *trans*-position. Alternatively, two imine-nitrogen atoms were located *cis* to one another, and two chlorine atoms, potential olefin polymerization sites, were also located *cis* to one another.

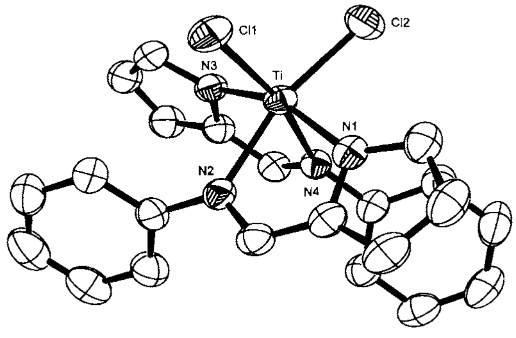


Figure 1. X-Ray Structure of complex 1. Selected bond distances (Å) and angles (°): Ti-Cl1 2.2506(7), Ti-Cl2 2.2598(6), Ti-N1 2.043(2), Ti-N2 2.215(2), Ti-N3 2.033(2), Ti-N4 2.185(2), Cl1-Ti-Cl2 97.82(3), N1-Ti-N2 75.50(6), N1-Ti-N3 158.04(6), N1-Ti-N4 87.60(6), N2-Ti-N3 87.12(6), N2-Ti-N4 80.54(5), N3-Ti-N4 76.22(6).

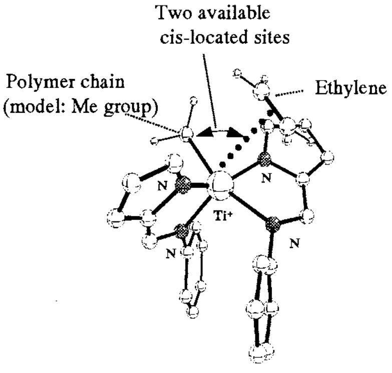


Figure 2. Calculated structure of the cationic species generated from neutral complex 1. Methyl group is employed as a model of a polymer chain.

An active species of group 4 transition metal complexes for olefin polymerization is known to be an alkyl cationic complex.[10] Thus, the structure of a methyl cationic complex generated from neutral complex **1** in the presence of ethylene was ascertained by DFT calculation (Figure 2).[11] In consequence, the cationic complex is suggested to possess two available *cis*-located sites needed for efficient olefin polymerization.

Subsequently, complexes **1** and **2** were investigated as ethylene polymerization catalysts using MAO as a cocatalyst at 25 °C under ethylene at atmospheric pressure (Table 1, entries 1 and 2).[12] Complex **1** furnished an activity of 6000 kg-polymer·mol-Ti^{-1}·h^{-1}. As far as we are aware, this is one of the highest activity values displayed by homogeneous titanium complexes with no Cp ligand(s) under the same polymerization conditions. The viscosity-average molecular weight (M_v) value of the polymer thus obtained was 7.5 × 10^4.[13] Interestingly, complex **2**, having a cyclohexyl group instead of the phenyl group, displayed 14100 kg-polymer·mol-Ti^{-1}·h^{-1} of activity with a very high M_v value of 260.1 × 10^4. This activity value, 14100 kg-polymer·mol-Ti^{-1}·h^{-1}, is comparable to that of Cp_2TiCl_2 (16700 kg-polymer·mol-Ti^{-1}·h^{-1}).

Alternatively, using $Ph_3C^+B^-(C_6F_5)_4/{}^iBu_3Al$ as a cocatalyst in the place of MAO, these complexes provided polyethylene which did not dissolve wholly in decalin solvent under the intrinsic viscosity measurement conditions, suggesting that the polyethylene thus obtained possesses exceptionally high molecular weight (Table 1, entries 4 and 5).[12,13]

Table 1. Polymerization results

Entry	Complex	Cocatalyst	Yield /g	Activity [a]	Mv /10^4
1	**1**	MAO	0.50	6000	7.5
2	**2**	MAO	1.18	14100	260.1
3	Cp_2TiCl_2	MAO	1.39	16700	125.3
4	**1**	$Ph_3C^+B^-(C_6F_5)_4/{}^iBu_3Al$	0.16	1900	473.9[b]
5	**2**	$Ph_3C^+B^-(C_6F_5)_4/{}^iBu_3Al$	0.17	2000	402.9[b]
6	Cp_2TiCl_2	$Ph_3C^+B^-(C_6F_5)_4/{}^iBu_3Al$	0.29	3500	77.3

Conditions; 25 °C, 0 .1 MPa pressure, toluene 250 ml,
Polymerization time; 5 min. Ethylene gas flow; 100 L / h.
Complex; 1 μmol. Cocatalyst; MAO (produced by Albemarle) ; 1.25 mmol, $Ph_3C^+B^-$ $(C_6F_5)_4$; 6 μmol, $^iBu_3Al$; 0.25 mmol.
[a] /kg-polymer·mol-Ti^{-1}·h^{-1}. [b] Polymer did not dissolve wholly in decalin under the intrinsic viscosity measurement conditions. These values were obtained from the polyethylene soluble in decalin under the intrinsic viscosity measurement conditions.

In summary, two new titanium complexes having two pyrolide-imine ligands were introduced. These complexes exhibited high ethylene polymerization activity using MAO or $Ph_3C^+B^-(C_6F_5)_4/{}^iBu_3Al$ as cocatalysts. These results together with our previous reports suggest that both titanium and zirconium complexes bearing multidentate and non-symmetric ligands have high potential as highly active new olefin polymerization catalysts.[4,6a]

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9 Complex **1**: ^1H-NMR (270 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.0–7.9 (m, 6H(pyrrole ring)+10H(benzene ring); aromatic-H), 7.80 (s, 2H; CH=N). Anal. Found: C, 58.29; H, 3.95; N, 12.62%. Calcd for $C_{22}H_{18}N_4TiCl_2$: C, 57.80; H, 3.97; N, 12.25%. FD-mass: *m/z*: 456 (M^+). Crystal data for complex **1**: Formula $C_{22}H_{18}N_4Cl_2Ti$, FW = 457.22, monoclinic, $P2_1/n$, $a = 11.606(2)$, $b = 14.200(2)$, $c = 14.294(2)$ Å, $\beta = 113.59(1)°$, $V = 2158.9(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.407$ g/cm^3, $T = 296$ K, 5175 unique reflections, $R(Rw) = 0.031(0.029)$. Complex **2**: ^1H-NMR (270 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.7–2.7 (m, 22H; cyclohexyl-H), 6.2–7.9 (m, 6H; aromatic-H), 8.00 (s, 2H; CH=N). Anal. Found: C, 56.79; H, 6.71; N, 12.12%. Calcd for $C_{22}H_{30}N_4TiCl_2$: C, 56.31; H, 6.44; N, 11.94%. FD-mass: *m/z*: 468 (M^+). Crystal data for complex **2**: Formula $C_{22}H_{18}N_4TiCl_2$, FW = 469.31, monoclinic, $P2_1/c$, $a = 14.064(9)$, $b = 11.446(2)$, $c = 14.354(2)$ Å, $\beta = 92.06(3)$, $V = 2309(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.350$ g/cm^3, $T = 150$ K, 4699 unique reflections, $R1 = 0.058$ (for 4496 data with $I > 2\sigma(I)$), $R(Rw) = 0.114(0.166)$. Single crystals of the titanium complexes **1** or **2** suitable for X-ray analysis were grown from a saturated hexane / CH_2Cl_2 solutions.

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11 DFT calculation has been widely used for structural determination of transition metal complexes, cf.; 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 electronic configuration of molecular system described by a triple -ζ basis set on the metal center. A double -ζ basis set was used for ethylene as a monomer and methyl group as a model of polymer chain. For the other atoms, a single -ζ basis set was used.

12 General polymerization procedure: Flow of ethylene gas was charged into toluene with vigorous stirring. To this solution, MAO and a toluene solution of a complex was added. In the case of $Ph_3C^+B^-(C_6F_5)_4/{}^iBu_3Al$ cocatalyst system, $^iBu_3Al$, complex solution, $Ph_3C^+B^-(C_6F_5)_4$ were added, in this order, to the solution.

13 M_v values were calculated from the following equation, $[\eta] = 6.2 \times 10^{-4} M_v^{0.7}$; R. Chiang, *J. Polymer Sci.*, **36,** 91 (1959). Intrinsic viscosity [η] was measured in decalin at 135 °C using an Ubbelohde viscometer. Preparation of intrinsic viscosity measurement solution; 25 mg of polyethylene was dissolved into 25 mL of decalin at 135 °C.