Unusual Enhancement of Ethylene Polymerization Activity of Benzyl Zirconium Complexes by Benzylation of the Imino Moiety of 2-(*N*-Aryliminomethyl)pyrrolyl Ligand

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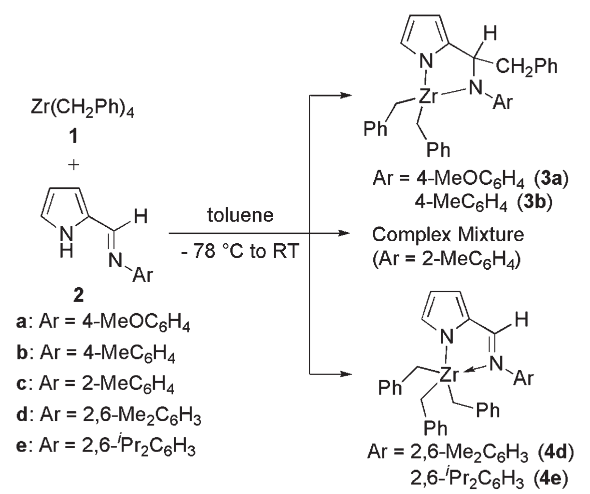
Reaction of $Zr(CH_2Ph)_4$ (**1**) with one equiv. of 2-(*N*-aryliminomethyl)pyrrolyl ligands (**2a**–**e**) in toluene afforded two types of products, depending upon the bulkiness of the aryl moiety. The reactions of **1** with two equiv. of the most sterically bulky **2e** afforded complex **5e**, whose pseudo octahedral geometry around the zirconium atom and totally dissymmetric *cis*-dibenzyl structure were elucidated. The high catalytic activity for ethylene polymerization was obtained by using complexes **3a** and **3b**.

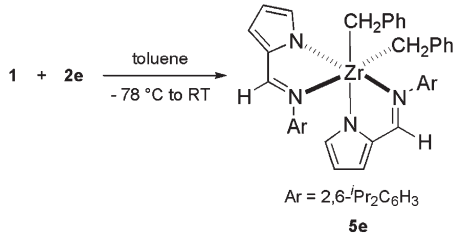
Homogeneous polymerization catalysis has been extensively studied in recent years.[1] In addition to metallocene-based catalysts of Group 4 metals, various transition metal complexes with nitrogen-based ligands such as 1,4-diaza-1,3-dienes,[2] bis(imino)pyridines,[3–5] phenoxy-imines,[6–9] and pyrrolyl-imines[10–13] have attracted much interest in terms of tunable and more flexibly designable ancillary ligands. It has recently been highlighted that phenoxy-imine complexes of titanium and zirconium have exhibited ultra-high catalytic activity[6] and also catalyzed the living polymerization of α-olefins.[6] Some of these catalysts bearing imino-derivatives, however, have been reported to show shorter lifetime due to the deactivation of the catalysts through the migratory insertion reaction of alkyl group bound to the metal center to the C=N moiety of the ligand.[5,9] We herein report unique enhancement, the inverse tendency, of catalytic activity for ethylene polymerization by the alkylation of the imino moiety of 2-(*N*-aryliminomethyl)pyrrolyl ligand bound to the zirconium center.

Scheme 1 shows the preparation of zirconium pyrrolyl-imine complexes starting from $Zr(CH_2Ph)_4$ (**1**). Two types of zirconium complexes were prepared by the reactions of **1** with one equiv. of 2-(*N*-aryliminomethyl)pyrrolyl ligands (**2a**–**e**) in toluene. Complexes **3** and **4** were selectively obtained depending on the bulkiness of aryl group of **2**. Reactions of **1** with less bulky ligands such as **2a** and **2b** gave dibenzyl complexes **3a** and **3b**, respectively, with the benzylation of the C=N moiety and the release of one equiv. of toluene. On the other hand, the reactions of **1** with 2,6-dialkyl substituted ligands **2d** and **2e** afforded tri(benzyl) complexes **4d** and **4e**, respectively, with the release of toluene. The substituenets at ortho-positions prevented the alkylation of the imino group. In the case of *o*-tolyl ligand **2c**, the reaction resulted in the complicated mixture, from which any product was not isolated. The complexes **3a** and **3b** were characterized by their ^1H NMR spectra, which displayed three sets of the benzyl signals. One ABX signal (δ 2.03 and 3.18 for **3a**; δ 2.04 and 3.15 for **3b**) is assignable to the $PhC\underline{H}_2CH$ group, while the other two sets are observed as AB*q* pattern at higher field (δ 1.31 and 1.96; δ 2.45 and 2.79 for **3a**: δ 1.30 and 1.96; δ 2.47 and 2.80 for **3b**) due to the benzyl groups bound to the zirconium atom. In sharp contrast, the ^1H NMR spectra of **4d** and **4e** showed only one singlet at δ 2.13 for **4d** and δ 2.18 for **4e** due to magnetically equiv. three CH_2 of the benzyl groups bound to the zirconium atom.



Scheme 1.

The reactions of **1** with two equiv of **2** were also conducted in similar condition. The most sterically bulky ligand **2e** afforded a complex **5e** (Eq 1), otherwise the reactions with **2a**–**d** did not give any isolable compounds due to the formation of the complicated reaction mixture. The complex **5e** was characterized by spectral data and X-ray analysis.[14] The ^1H NMR spectra of the complex **5e** showed one singlet due to benzyl group at room temperature; however, two broad signals were observed below 263 K, indicating that dissymmetrical structure. The coalescence of the benzyl resonances allowed to estimate the energy parameters for the interconversion process to be $\Delta G^{\ddagger} = 12.6\,\mathrm{kcal/mol}$. Figure 1 shows the pseudo octahedral geometry around the zirconium atom and a *cis*-arrangement of two benzyl groups suitable for the catalyst of the ethylene polymerization. It is of particular interest that one benzyl group is *trans* to the nitrogen atom of the imino group, while the other is *trans* to the nitrogen atom of the pyrrolyl moiety, being consistent with NMR spectroscopy. This is in contrast to the reported C_2-symmetric geometry found for dichloro complexes of titanium[13] and zirconium,[11] a diamido complex of zirconium,[12] and a dibenzyl hafnium complex[13] bearing pyrrolyl-imine ligands. The ipso carbon of one benzyl group interacted with the zirconium atom as evident from the shorter distance of Zr-C2 (2.760(2) Å) and the smaller angle of Zr-C1-C2 (91.9(1)°).



(1)

Ar = 2,6-$^iPr_2C_6H_3$

5e

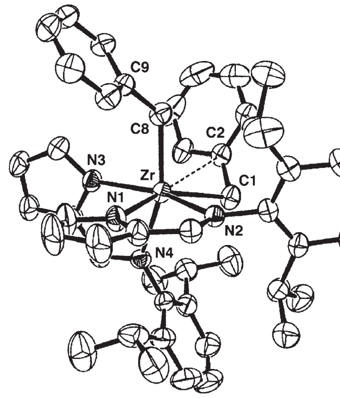


Figure 1. Crystal Structure of **5e**.

Table 1 summarizes the results of ethylene polymerization using mono- and bis[2-(*N*-aryliminomethyl)pyrrolyl] zirconium complexes **3**–**5** as catalyst precursors. All these zirconium complexes exhibited catalytic activity for ethylene polymerization under atmospheric pressure of ethylene in the presence of excess (1000 equiv.) amounts of MMAO. The catalyst precursor with the highest activity was the complex **3b**; the activity of ethylene polymerization within 5 min at 0 °C was found to be 1.08×10^3 kg-PE/mol-cat·h (Run 2). Comparable high activity (0.8×10^3 kg-PE/mol-cat·h) was obtained for the polymerization using **3a** (Run 1). It is noteworthy that these complexes are pyrrolyl-amido complexes, whereas **4d** and **4e**, which have the tribenzyl zirconium center supported by one (iminomethyl)pyrrolyl ligand, exhibited 10^2 less catalytic activities (Run 5 and 6), being in sharp contrast to the reported deactivation caused by the alkylation of the imino moiety of phenoxy-imine[9] and by the alkylation of pyridine ring of bis(iminomethyl)pyridine[5] bound to the catalyst center. Thus, this is the first example of the enhancement by such the alkylation of the imino moiety of the ligands. The polymerizations conducted with **3b** at higher temperature (25 and 60 °C, Run 3 and 4) resulted in the lower activities, indicating that the complex **3b** is thermally unstable in the polymerization condition due to coordinative unsaturation around the zirconium center. We assumed that high unsaturation around the zirconium center was compensated by the interaction with the phenyl group of the armed-pendant in **3a** and **3b**, as similar to the pendant phenyl group attached to the Cp ligand that reversibly interacted with the cationic zirconium center.[15,16]

The dibenzyl zirconium complex **5e** exhibited a low catalytic activity equal to those found for **4d** and **4e**, but the obtained polyethylene had a very broad M_w/M_n value, presumably due to the gradual formation of catalytic active species (Run 7). This suggested that the *cis*-dialkyl zirconium center having bulky ligands did not readily generate a catalytically active cationic monoalkyl species, but the replacement of the chelating ligand might be the first step to initiate the polymerization.

Table 1. Polymerization of ethylene catalyzed by zirconium complexes[a)]

Run	Cat.	Time /min	Temp. /°C	A[b)]	M_w ($\times 10^3$)	M_w/M_n
1	**3a**	5	25	810	3.0	2.5
2	**3b**	5	0	1084	3.8	2.2
3	**3b**	5	25	916	7.9	2.8
4	**3b**	5	60	419	4.9	2.2
5	**4d**	60	25	19	—	—
6	**4e**	60	25	51	—	—
7	**5e**	90	25	21	94	28.4

a) Conditions: [cat.] = 1 mM in toluene, ethylene pressure = 1 atm, and [cocatalyst] = 1000 equiv of MMAO. b) A = Activity (kg-PE/mol-cat·h).

In summary, we demonstrated that 2-(*N*-aryliminomethyl)-pyrrolyl ligands reacted with one equiv of $Zr(CH_2Ph)_4$ (**1**) to give two kinds of pyrrolyl-amido complexes **3** and pyrrolyl-imine complexes **4**, while the reaction of **1** with two equiv. of **2e** resulted in the formation of a bis[(iminomethyl)pyrrolyl]zirconium complex **5e**. In the case of complexes **3**, the benzylation of the imino moiety of the ligand dramatically enhanced the ethylene polymerization activity. Investigation on unique catalyst activation by the alkylation of the imino moiety is in progress.

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14 Crystal data for **5e**: $C_{48}H_{56}N_4Zr$, Orthorhombic, space group $Pna2_1$ (No. 33), $a = 23.1021(5)$ Å, $b = 17.3933(4)$ Å, $c = 10.5947(3)$ Å, $V = 4257.2(2)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.217\,\text{g cm}^{-3}$, $T = 233(1)$ K, Rigaku R-AXIS RAPID, Mo Kα radiation ($\lambda = 0.71069$), $\mu = 0.295\,\text{mm}^{-1}$, numerical absorption correction (0.9586–0.9862). The full-matrix least squares refinement on F^2 with all 13510 reflections and 645 variables converged to $R_1 = 0.0576$ (all data), $wR_2 = 0.0881$ (all data), Flack parameter (χ) $= -0.01(2)$, GOF $= 1.081$, and $\Delta\sigma_{(\max)} = 0.004$.

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