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IN SITU GENERATION OF CATIONIC METHYLZIRCONIUM COMPLEXES FROM *rac*-(EBI)Zr(NMe_2)$_2$ AND NMR-SCALE POLYMERIZATION OF PROPYLENE

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Key Words: Metallocene Amide, Activation, NMR-Scale Reaction, Cationic Zirconium Species, Propylene Polymerization

ABSTRACT

Sequential NMR-scale reactions have been carried out in order to generate cationic methylzirconium complexes by the reaction of *rac*-(EBI)Zr(NMe_2)$_2$ (*rac*-1, EBI = Et(indenyl)$_2$) with methylaluminoxane (MAO) or various anionic compounds. By reacting 40 equiv. of MAO with *rac*-1 in an NMR tube containing CD_2Cl_2 as a solvent at room temperature, *rac*-1 *is* completely activated to give stable cationic methylzirconium complexes, $[(EBI)ZrMe]^+[MAO]^-$ which polymerize propylene to isotactic polypropylene (*i*PP). The formation of the cationic species is achieved after *rac*-1 *is* methylated to form *rac*-(EBI)$ZrMe_2$ (*rac*-2) by MAO and/or free Al_2Me_6 contained in MAO. The same sequential reaction has been performed by using *rac*(EBI)$ZrCl_2$ (*rac*-3) for the comparison. MAO cannot generate the cationic species at the same reaction conditions in the reaction of *rac*-3 and MAO, mainly due to the difficulties of methylation of *rac*-3. *Ansa* ziconocene amide *rac*-1 *is* stoichiometrically methylated by 2 equiv. of Al_2Me_6 to give *rac*-2. Introduction of 1 equiv. of noncoordinating to the solution mixture of *rac*-1 and 2 equiv. of Al_2Me_6 leads to the formation of stable cationic methylzirconium species, [*rac*-(EBI)Zr(μ-Me)$_2$AlMe$_2$]$^+$. NMR-scale polymerizations have been carried out by adding a small amount of liquid propylene to these cationic species. The meso pentad values of *i*PP isolated in these polymerizations are in the range of 80.2-84.7%. By changing the order of sequential reaction, i.e., by reacting *rac*-**1** with noncoordinating anions prior to methylation by Al_2Me_6, the yield to give cationic methylzirconium species is decreased. Coordinative anions such as [$HNMe_2Ph$][BPh_4] and [$HNBu_3$][BP_4] are less effective for the generation of the active zirconium cations than noncoordinating anions. The amount of MAO needed to activate *rac*-**1** can be decreased by the pre-methylation of *rac*-**1** by Al_2Me_6.

INTRODUCTION

It is well established that a cationic complex, [Cp_2MR]$^+$, is the active species of Group 4 metallocene/MAO catalysts and related systems in olefin polymerization [1]. The excess MAO presumably functions partly as a Lewis acidic precursor of a poorly coordinating anion, and so alternative anions are of interest for single-site catalysts [2-5]. The cationic species were usually generated by the reaction of Cp_2MR_2, prepared by alkylation of corresponding halide compounds or by the metallation of ligand with MR_4, together with various cocatalysts. The yield to get Group 4 *ansa*-metallocene complexes which are highly effective for the stereo-specific polymerization of α–olefin is low, and tedious isomer separation and purif-ication steps are accompanied. Recently, Jordan *et al.* [6] invented a new method to prepare racemic *ansa*-metallocene amide complexes selectively with a very high yield via an amine elimination route. In the previous study [6c], the *ansa*-metallocene amide complexes have been demonstrated to be active for the propylene polymerization by adopting various cocatalyst formulations. In this study, the detailed activation procedures of *rac*-(EBI)Zr(NMe_2)$_2$ have been described by using MAO or anionic compounds as coactivators. The activation procedures of conventional halide complex *rac*-(EBI)$ZrCl_2$ are also investigated for the comparison.

EXPERIMENTAL

Materials

Polymerization grade propylene (Matheson Co.) was purified by passing it through columns of Fisher RIDOX catalyst and molecular sieve 5A/13X. $AlMe_3$ was obtained from Aldrich and used without purification. MAO was donated by

Albemarle as a 10% solution in toluene, which contained 1.85 wt% $AlMe_3$ and 8.15 wt% MAO (4.49 wt% total Al). *Ansa*-zirconocene complexes 1 and 3 were synthesized according to previous procedures [6]. Various anionic complexes, $[HNMe_2Ph][B(C_6F_5)_4]$, $[HNMePh_2][B(C_6F_5)_4]$, $[Ph_3C][B(C_6F_5)_4]$, $[HNEt_2Ph][B(C_6F_5)_4]$, $[HNMe_2Ph][BPh_4]$, and $[HNBu_3][BPh_4]$ were also prepared by literature procedures [3, 5, 6].

Methods

The procedure for *in situ* generating solutions of zirconium cationic species in an NMR tube by the sequential reaction of *rac*-1, $AlMe_3$, and $[HNMePh_2]$-$[B(C_6F_5)_4]$ is exemplified below. The *rac*-1, (20 mg, 45.9 μmol) was dissolved in CD_2Cl_2 (0.5 mL) at room temperature to give a red solution. In a dry box prescribed amount of $AlMe_3$ was sequentially added to the solution mixture for the methylation of *rac*-1. Addition of 4 equiv. of $AlMe_3$ resulted in an orange solution. After analyzing the solution mixture, $[HNMePh_2][B(C_6F_5)_4]$ (39 6 mg, 45 9 μmol) was introduced into the NMR tube at room temperature to generate methylzirconium cations. The color of the solution mixture immediately changed from orange to light yellow. After analysis, about 0.5 mL of liquid propylene was added to the mixture at -78°C, followed by slowly increasing the temperature to room temperature. Solid *i*PP formed in this NMR scale polymerization was isolated and dried for the analysis.

NMR spectra were obtained with a Bruker AMX-360 and WM-300 spectrometer. Samples for ^{13}C NMR spectra were prepared by dissolving 50 mg of polymer in 0.5 mL of C_6D_6/1,2,4-trichlorobenzene (1/5) and were measured at 120 °C.

RESULTS AND DISCUSSION

To determine whether the *ansa*-metallocene diamide compound is activated for the propylene polymerization by conventional procedures, sequential reactions of *rac*-1 with MAO has been performed in an NMR tube. By sequentially increasing the amount of MAO from MAO/*rac*-1 = 10 to 40, ^1H NMR spectrum of each solution mixture was recorded. Table 1 summarizes the chemical shifts of *rac*-1 and the identified compounds contained in the solution mixtures obtained by the reaction of *rac*-1 with MAO in different proportions (MAO/*rac*-1 = 10, 20 and 40). The relative composition of identified compounds is also indicated in Table 1. By increasing the amount of MAO from 10 equiv. to 40 equiv., NMe_2 in *rac*-1 is first

TABLE 1. The Chemical Shifts of Various Compounds and Reaction Mixtures[1]

Compounds or reaction mixtures	Identified Compounds	CR[2)]	Chemical shifts (δ), identified (ppm)
rac-(EBI)Zr $(NMe_2)_2$			7.69 (d, 2H, indenyl), 7.48 (d, 2H, indenyl), 7.06 (dd, 2H, indenyl), 6.80 (dd, 2H, indenyl), 6.39 (d, 2H, C_5 indenyl), 6.06 (d, 2H, C_5 indenyl), 3.71 (m, 2H, CH_2), 3.50 (m, 2H, CH_2), 2.43 (s, 12H, NMe_2)
$[HNMePh_2]$ $[B(C_6F_5)_4]$			8.80 (s, 1H), 7.64 (m, 6H), 7.41 (m, 4H), 3.83 (s, 3H)
$[Ph_3C]$ $[B(C_6F_5)_4]$			8.27 (t, 3H), 7.87 (t, 6H), 7.66 (d, 6H)
Al_2Me_6			-0.29 (s)
rac-(EBI)Zr$(NMe_2)_2$/ 10 MAO	rac-(EBI)Zr $(NMe_2)_2$	1	7.69 (d, indenyl), 7.06 (dd, indenyl) 6.80 (dd, indenyl), 6.40 (d, C_5 indenyl), 6.06 (d, C_5 indenyl), 2.43 (s, NMe_2)
	rac-(EBI)ZrMe(NMe_2)	1	6.89 (pseudo t, indenyl), 6.31 (d, C_5 indenyl), 6.13 (d, C_5 indenyl), 6.10 (d, C_5 indenyl), 5.84 (d, C_5 indenyl), 2.31 (s, NMe_2), -1.20 (s, Zr-CH_3)
	rac-(EBI)ZrMe_2	2	7.48 (d, indenyl), 7.06 (pseudo t, indenyl), 6.01 (d, C_5 indenyl), -1.42 (s, Zr-CH_3)
	$[(EBI)ZrMe]^+$	3	8.10 (d, indenyl), 7.63 (d, indenyl), 7.41 (dd, indenyl), 6.54 (d, C_5 indenyl), 6.50 (d, C_5 indenyl), 3.90 (m, CH_2), -0.67 (s, Zr-CH_3)
	$Al_2Me_4(NMe_2)_2$		2.39 (s, NMe_2), -0.79 (s, Al-CH_3)
	MAO		MAO could not be interpreted. Free $AlMe_3$ in MAO was transformed to $Al_2Me_4(NMe_2)_2$.
rac-(EBI)Zr$(NMe_2)_2$/ 20 MAO	rac-(EBI)ZrMe_2	1	7.48 (d, indenyl), 7.06 (pseudo t, indenyl), 6.01 (d, C_5 indenyl), -1.42 (s, Zr-CH_3)
	$[(EBI)ZrMe]^+$	4	8.10 (d, indenyl), 7.62 (d, indenyl), 7.58 (pseudo t, indenyl), 7.40 (pseudo t, indenyl), 6.54 (d, C_5 indenyl), 6.51 (d, C_5 indenyl), 3.90 (m, CH_2), -0.67 (s, Zr-CH_3)
	$Al_2Me_4(NMe_2)_2$ (6)		2.39 (s, NMe_2), -0.79 (s, Al-CH_3)
	$Al_2Me_5(NMe_2)$ (7)		2.40 (s, NMe_2), -0.54 (s, Al-CH_3); **6/7** ratio is measured to be 1/1 in this mixture.
	MAO		MAO could not be interpreted. Free $AlMe_3$ in MAO was transformed to **6** and **7**.
rac-(EBI)Zr$(NMe_2)_2$/ 40 MAO	$[(EBI)ZrMe]^+$		8.01(d, indenyl), 7.63 (d, indenyl), 7.58 (pseudo t, indenyl), 7.41 (pseudo t, indenyl), 6.54 (d, C_5 indenyl), 6.50 (d, C_5 indenyl), 3.90 (m, CH_2), -0.67 (s, Zr-CH_3)
	6, **7**		**6/7** ratio is measured to be 1/2 in this mixture.
	MAO		MAO could not be interpreted. Free $AlMe_3$ in MAO was transformed to **6** and **7**.
rac-(EBI)Zr$(NMe_2)_2$/ Al_2Me_6	rac-(EBI)Zr$(NMe_2)_2$	1	7.69 (d, indenyl), 6.80 (dd, indenyl), 6.39 (d, C_5 indenyl), 6.06 (d, C_5 indenyl), 2.43 (s, NMe_2)
	rac-(EBI)ZrMe_2	3	6.56 (pseudo t, indenyl), 6.01(d, C_5 indenyl), -1.42 (s, Zr-CH_3)
	rac-(EBI)ZrMe(NMe_2)	10	7.87 (d, indenyl), 6.89 (pseudo t, indenyl), 6.31 (d, C_5 indenyl), 6.13 (d, C_5 indenyl), 6.10 (d, C_5 indenyl), 5.84 (d, C_5 indenyl), 2.31 (s, NMe_2), -1.20 (s, Zr-CH_3)
	6, **7**		**6/7** ratio is measured to be 1/1 in this mixture.
rac-(EBI)Zr$(NMe_2)_2$/ 2 Al_2Me_6	rac-(EBI)ZrMe_2		7.48 (d, 2H, indenyl), 7.43 (d, 2H, indenyl), 7.19 (pseudo t, 2H, indenyl), 7.06 (pseudo t, 2H, indenyl), 6.56 (d, 2H, C_5 indenyl), 6.01 (d, 2H, C_5 indenyl), 3.35 (m, 2H, CH_2), 3.18 (m, 2H, CH_2), -1.42 (s, 6H, Zr-CH_3)
	6, **7**, Al_2Me_6		**6/7**/Al_2Me_6 ratio is measured to be 1/5/2 in this mixture.

TABLE 1. Continued

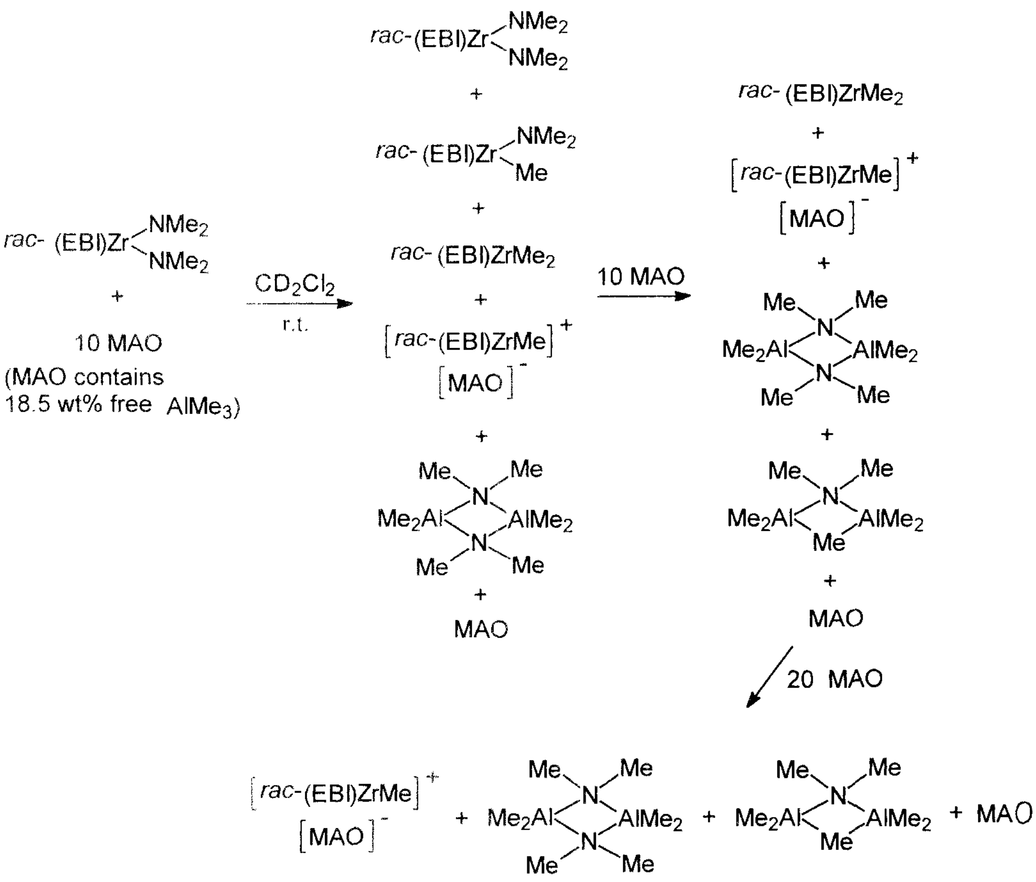
rac-(EBI)Zr$(NMe_2)_2$/ 2 Al_2Me_6/$[HNMePh_2]$ $[B(C_6F_5)_4]$	[rac-(EBI)Zr$(\mu\text{-}Me)_2$Al $Me_2]^+$		7.89 (br, indenyl), 6.45 (d, C_5 indenyl), 6.20 (d, C_5 indenyl), 4.03 (br, m, CH_2), 3.27 (br, m, CH_2), -0.63 (s, μ-CH_3), -0.58 (s, Al-CH_3)
rac-(EBI)Zr$(NMe_2)_2$/ 2 Al_2Me_6/$[Ph_3C]$ $[B(C_6F_5)_4]$	[rac-(EBI)Zr$(\mu\text{-}Me)_2$Al $Me_2]^+$		7.90 (d, indenyl), 7.33(pseudo t,indenyl), 6.45 (d, C_5 indenyl), 6.21 (d, C_5 indenyl), -0.62 (s, μ-CH_3), -0.57 (s, Al-CH_3)
rac-(EBI)Zr$(NMe_2)_2$/ $[HNMePh_2][B(C_6F_5)_4]$	(EBI)Zr$(NMe_2)^+$, $HNMe_2$ coordinated		7.99 (d, 1H, indenyl), 7.85 (d, 1H, indenyl), 7.63 (d, 1H, indenyl), 7.52 (d, 1H, indenyl), 7.44 (pseudo t, 1H, indenyl), 7.35 (m, 2H, indenyl), 7.17 (pseudo t, 2H, indenyl), 6.94 (pseudo t, 2H, indenyl), 6.59 (d, 1H, C_5 indenyl), 6.18 (d, 1H, C_5 indenyl), 6.14 (d, 1H, C_5 indenyl), 6.00 (d, 1H, C_5 indenyl), 4.06 - 3.63 (m, 4H, CH_2), 2.77 (s, 6H, NMe_2), 2.41 (d, 3H, $HNMe_2$), 2.08 (d, 3H, $HNMe_2$), -0.73 (br s, 1H, $HNMe_2$)
rac-(EBI)Zr$(NMe_2)_2$/ $[HNMePh_2][B(C_6F_5)_4]$/ 2 Al_2Me_6	(EBI)Zr$(NMe_2)^+$, $HNMe_2$ coordinated	10	7.99, 7.85, 7.63, 7.52 (d, indenyl), 7.44 (pseudo t, indenyl), 7.35 (m, indenyl), 7.17 (pseudo t, indenyl), 6.94 (pseudo t, indenyl), 6.59 (d, C_5 indenyl), 6.18 (d, C_5 indenyl), 6.14 (d, C_5 indenyl), 6.00 (d, C_5 indenyl), 4.06 - 3.63 (m, CH_2), 2.77 (s, NMe_2), 2.41 (d, $HNMe_2$), 2.08 (d, $HNMe_2$), -0.73 (br s, $HNMe_2$)
	$[(EBI)ZrMe]^+$, $HNMe_2$ coordinated	9	Only Zr-CH_3 signal was assigned. Signals in the indenyl region overlap because of the presence of various compounds. -0.967 (s, Zr-CH_3)
	[rac-(EBI)Zr$(\mu\text{-}Me)_2$Al $Me_2]^+$	1	-0.63 (s, Zr-CH_3), -0.58 (s, Al-CH_3)
	$Al_2Me_5(NMe_2)$		0.54 (s, Al-CH_3)

[1] Some chemical shifts of identified compounds are obscured by the interference of other compounds coexisted in solution mixtures.

[2] Composition ratio by ^{1}H NMR.

methylated by MAO and or free $AlMe_3$ contained in MAO, followed by activated to form cationic active species. By reacting *rac*-1 with 10 equiv. of MAO (MAO/*rac*-1 = 10), unreacted *rac*-(EBI)Zr$(NMe_2)_2$, *rac*-(EBI)Zr(NMe_2)(Me) (*rac*-4), *rac*(EBI)ZrMe_2, and cationic $[(EBI)ZrMe]^+[MAO]^-$ (5) species are observed as a ratio of 1, 1, 2, and 3, respectively. All free $AlMe_3$ contained in MAO is transformed to $Al_2Me_4(NMe_2)_2$ (6), demonstrating that methyl ligand in *rac*-(EBI)Zr(NMe_2)(Me), *rac*-(EBI)ZrMe_2, and cationic $[(EBI)ZrMe]^+[MAO]^-$ species originated from free $AlMe_3$ contained in MAO. By adding 10 more equiv. of MAO (MAO/*rac*-1 = 20) to the solution mixture, unreacted *rac*-1 and *rac*-4 are transformed to *rac*-2 and 5. In this solution mixture 5/*rac*-2 ratio is 4. By further increasing the amount of MAO to MAO/*rac*-1 = 40, *rac*-2 is completely activated to form cationic zirconium species, 5. Thus, the procedure for the formation of cationic zirconium species formed by the reaction of *rac*-1 with an excess amount of MAO can be summarized as shown in Scheme 1.

The structure of the cationic species and the nature of the interaction between MAO and zirconium cations under catalytic conditions, in other words in



Scheme 1

solution, remain uncertain, In order to confirm the formation of active complex 5, a small amount of liquid propylene was introduced into the NMR tube containing the reaction mixture (MAO/*rac*-1 = 40) at -78°C. White *i*PP was precipitated from the solution mixture by slowly increasing the temperature of reaction mixture to room temperature. The meso pentad (mmmm) value of *i*PP isolated from the NMR tube was 80.2%.

Interestingly, the analogous compound *rac*-(EBI)ZrC12 (*rac*-3) could not be activated at the same reaction conditions. By reacting *rac*-3 with the same amount of MAO (MAO/*rac*-3 = 40) no conspicuous methyl hydrogen peaks representing the formation *rac*-2 and 5 were observed. Even after increasing the reaction temperature to 70°C or increasing the amount of MAO (MAO/*rac*-3 = 100), the chemical species *rac*-2 and 5 were not observed. By reacting *rac*-3 with 100 equiv. of MAO only 10% of *rac*-3 was transformed to racEBI)Zr(Cl)(Me) and 90% of *rac*-3 remained unreactive. These results demonstrate that the activation of *rac*-3 is more difficult than that of *rac*-1, presumably due to the difference in methylation by MAO.

The flexibility of methylation of *ansa*-metallocene amide *rac*-1 can be directly demonstrated by the reaction of *rac*-1 with $AlMe_3$ at room temperature. Table 1 shows chemical shifts of the reaction mixtures obtained by the reaction of *rac*-1 with various amounts of $AlMe_3$. As the amount of $AlMe_3$ increases from Al_2Me_6/*rac*-1 = 1 to 2, *rac*-1 is partly methylated to form *rac*-4 and then completely methylated to form *rac*-2. This methylation reaction occurred stoichiometrically (Equation 1).

$$rac\text{-}(EBI)Zr(NMe_2)_2 + Al_2Me \rightarrow rac\text{-}(EBI)Zr(NMe_2)(Me) + Al_2Me_5(NMe_2)(\underline{7}) \quad (1)$$

$$rac\text{-}(EBI)Zr(NMe_2)(Me) + Al_2Me_6 + Al_2Me_5(NMe_2) \rightarrow rac\text{-}(EBI)ZrMe_2 + Al_2Me_5(NMe_2) \quad (2)$$

Part of $Al_2Me_5(NMe_2)$ seems to be transformed into $Al_2Me_4(NMe_2)_2$,

$$2\,Al_2Me_5(NMe_2) \leftrightarrows Al_2Me_6 + Al_2Me_4(NMe_2)_2 \quad (3)$$

In the reaction mixture of 1 with 2 equiv. of Al_2Me_6 three kinds of dimeric methylaluminum compounds, $Al_2Me_5(NMe_2)$, Al_2Me6, and $Al_2Me_4(NMe_2)$2, are observed with the ratio of 5, 2, and 1, respectively.

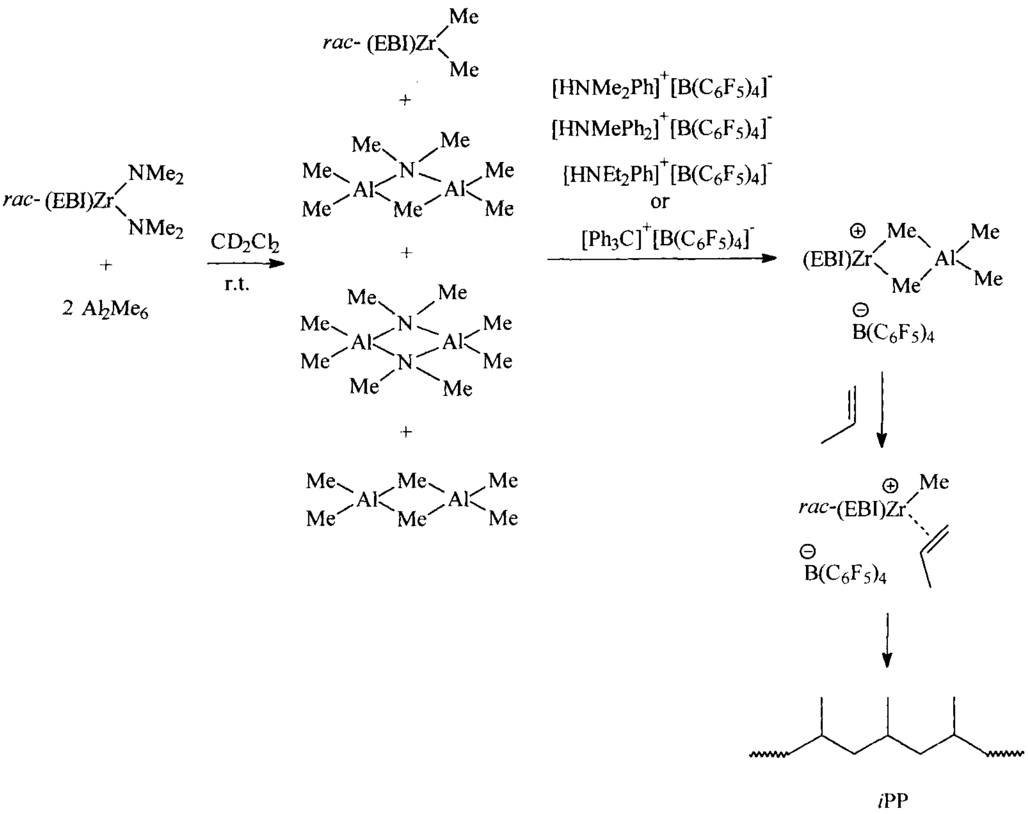
In contrast with most MAO-containing catalyst systems, which start with metallocene dichloride complexes such as Cp_2ZrCl_2, non-aluminoxane-containing catalyst systems can start from alkylated metallocene complexes such as Cp_2ZrR_2 and avoid the alkylation requirement. As substitutes for MAO, bulky anions are used to stabilize cationic metallocene complexes in order to maintain their reactivity. The bulky anion must be noncoordinating and must be chemically very stable so that it does not react with the highly reactive metallocene cation. As the most effective bulky anions for the generation of metallocene cations, noncoordinating anions such as $[HNMe_2Ph][B(C_6F_5)_4]$, $[HNMePh_2][B(C_6F_5)_4]$, and $[Ph_3C][B(C_6F_5)_4]$ have been used. In order to use dichloride metallocene compound *rac*-3 for the generation of cationic zirconium species by the reaction of the bulky anions, *rac*-3 must be previously alkylated in a separate synthetic process to get *rac*-$(EBI)ZrR_2$. However, since $AlMe_3$ can stoichiometrically methylates corresponding metallocene amide compound *rac*-1 , it can be directly activated to form methylzirconium cations by using non-aluminoxanes during polymerization.

In order to prove this fact, sequential reactions have been carried out by using *rac*-1, $AlMe_3$, and various noncoordinating anions in an NMR tube. Table 1 summarized the chemical shifts of identified chemical species obtained from these sequential reactions. Addition of 1 equiv. of $[HNMePh_2][B(C_6F_5)_4]$ to the solution (Al_2Me_6/*rac*-1 (2/1)) containing *rac*-2 previously methylated according to Equations 1 and 2, results in an immediate formation of [*rac*-(EBI)Zr(μ-Me)$_2$AlMe$_2$]$^+$ (8), the adduct of the base-free *rac*-[(EBI)ZrMe]$^+$ cation and $AlMe_3$ was previously identified by Bochmann [1(g)] as the principal component in mixtures of these species. The resonance of 8 and the Al amide species are broadened, presumably due to the reversible formation of $NMePh_2$ adducts. Cationic complex 8 may undergo loss or displacement of $AlMe_3$, ultimately leading to *rac*-[(EBI)ZrMe]$^+$ or *rac*-[(EBI)Zr(Me)(propene)]$^+$ species. This was indirectly confirmed by the NMR-scale polymerization of propylene. Liquid propylene (0.5 mL) was added to the mixture containing 8 at -78°C, and then slowly increased the temperature to room temperature. White *i*PP showing meso pentad value of 84.7% was isolated in this procedure.

Similarly, sequential reactions of *rac*-1 with 2 equiv. of Al_2Me_6 and then 1 equiv. of $[Ph_3C][B(C_6F_5)_4]$ resulted in the formation of the same cationic species 8 as a stoichiometric NMR yield as shown in Table 1. In the same NMR-scale polymerization these cationic zirconium species polymerizes propylene to give *i*PP (mmmm = 84.3%). The same cationic species 8 could also be generated by using $[HNMe_2Ph][B(C_6F_5)_4]$ and $[HNEt_2Ph][B(C_6F_5)_4]$ as non-coordinating anions. The formation of base-free methylzirconium cations by non-coordinating anions can thus be summarized as shown in Scheme 2.

The solution mixture containing cationic complex the temperature 8 is very stable, so that the mixture was not decomposed after storing for about a month at room temperature and even after heating to 70°C for 3 hours. The structure of 8 in solution is assumed to be different from that of cationic species 5 generated by using MAO as an anion. As shown in Table 1, the chemical shift of methyl in 8 is -0.63 ppm, on the other hand, that of 5 is -0.67 ppm.

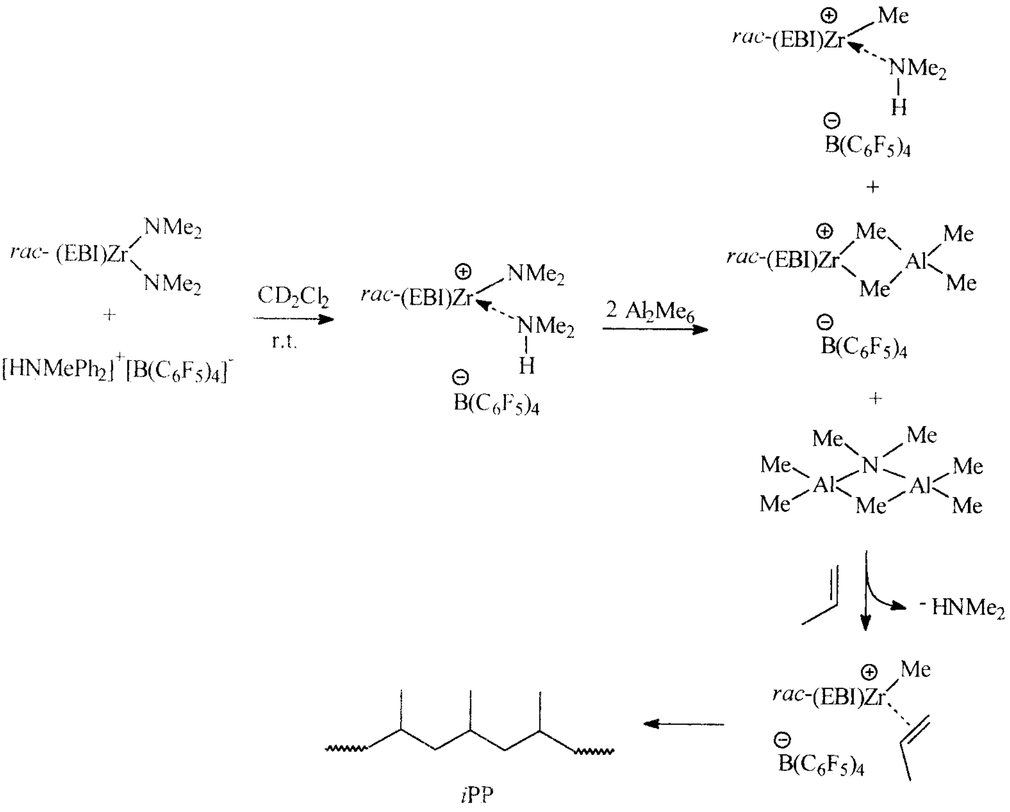
Since MAO-containing catalyst systems may also start with the alkylated metallocene complex, a different amount of MAO was introduced into the solution mixture (Al_2Me/*rac*-1 = 2/1) containing *rac*-2. With 10 equiv. of MAO 65% of *rac*-2 was activated to give 5 , and 10 more equiv. of MAO was enough to completely activate *rac*-2. These results demonstrate that relatively less amount of



Scheme 2

MAO is needed for the activation of *rac*-1 if it is preliminarily methylated by $AlMe_3$ (compare with *rac*-1/MAO system in Table 1). In this way, the amount of MAO required for the activation of *rac*-1 can be decreased. The meso pentad value of *i*PP obtained from the NMR-scale polymerization of propylene with *rac*-1/Al_2Me_6/MAO (1/2/20) systems was 80.4%, which is a similar value of *i*PP obtained by *rac*-1/MAO (1/40) systems.

In a *rac*-1/2Al_2Me_6/non-coordinating anion system, cationic 8 is formed via the prior methylation of *rac*-1 by Al_2Me_6. Thus, it is expected that changing the reaction order of the three reactants changes the formation procedure of the cationic species. In order to confirm this, *rac*-1 was first reacted with $[HNMePh_2][B(C_6F_5)_4]$ prior to methylate *rac*-1 with Al_2Me_6. The chemical shifts of the identified chemical species contained in the solution mixture are summarized in Table 1. As expected, cationic Zr species containing an amide as a ligand



Scheme 3

$[(EBI)Zr(NMe_2)]^+$ (9) are formed. NMR-scale polymerization of propylene has been tried by adding liquid propylene to the solution mixture containing 9, results in no *i*PP. This is because the nitrogen atom of $HNMe_2$ generated as a byproduct in this reaction is strongly coordinated to the Zr center. The cationic species 9 were subsequently methylated with 2 equiv. Al_2Me_6 to generate cationic methylzirconium cations. However, NMe_2 ligand in 9 is not completely transformed to the methyl group to form cationic $[(EBI)ZrMe]^+$ species, i.e., about 50% of it remains unreacted, presumably due to the strong coordination of $HNMe_2$ to the metal center. $HNMe_2$ remains coordinated to Zr center in cationic $[(EBI)ZrMe]^+$ species and small amount of [*rac*-$(EBI)Zr(\mu Me)_2AlMe_2]^+$ is also formed as shown in Table 1 . Liquid propylene monomer was introduced into NMR tube containing these cationic species. In this procedure, part of $HNMe_2$ coordinated to Zr is replaced by propylene to give $[(EBI)Zr(Me)(propene)]^+$ species. These species polymerize propylene to give *i*PP showing meso pentad value of 81.9%. The procedure for the generation of cationic active species by the sequential reaction of *rac*-1/[HNMePh$_2$][B(C$_6$F$_5$)$_4$/2Al$_2$Me$_6$ can thus be summarized as shown in Scheme 3, even if the yield to give [(EBI)Zr(Me)(propene)]$^+$ species is not very high in comparison with *rac*-1/2Al$_2$Me/[HNMePh$_2$][B(C$_6$F$_5$)$_4$] system.

In order to compare the performance of the activator, similar NMR-scale reactions have been carried out by using coordinating anions such as [HNMe$_2$Ph][BPh$_4$] and [HNBu$_3$][BPh$_4$]. After completely methylating *rac*-1 by 2 equiv. of Al$_2$Me$_6$, each coordinating anion was added to the reaction mixture at room temperature. By using [HNMe$_2$Ph][BPh$_4$] as a coactivator, only 2% of *in situ* generated *rac*-2 is activated to form base-free methylzirconium cations, 8. By reacting [HNBu$_3$][BPh$_4$] with the same mixture (Al$_2$Me$_6$/ *rac*-1 = 2), about 75% of *rac*-2 is activated to give cationic zirconium species 8, demonstrating that [HNBu$_3$][BPh$_4$] is much more effective than [HNMe$_2$Ph][BPh$_4$] as a cocatalyst to generate 8. These results suggest that a considerable amount of [BPh$_4$] anions is not coordinated to the zirconium, but instead is present as a mixture of solvated and ion paired species. If we compare noncoordinating anions with coordinating anions as coactivators to give cationic active species, the coordinating strength and the structure of the anions seems to be a very important factor.

CONCLUSION

Ansa-metallocene amide compound *rac*-1 was completely activated to give [(EBI)ZrMe]$^+$ MAO]$^-$ species by reacting with 40 equiv. of MAO in an NMR-scale reaction at room temperature. The formation of the cationic species is achieved after *rac*-1 *is* methylated by MAO and/or free Al$_2$Me$_6$ contained in MAO. The same cationic species are not obtained with corresponding dihalide compound, *rac*-3, at the similar reactions with MAO mainly due to the difficulty of methylation. The methylation of *rac*-1 *is* stoichiometrically achieved by Al$_2$Me$_6$ to give *rac*-2. By adding 1 equiv. of noncoordinating anions to the reaction mixture (*rac*-1/2 Al$_2$Me$_6$) containing *rac*-2, base-free methylzirconium cations, [*rac*-(EBI)Zr(μ-Me)$_2$AlMe$_2$]$^+$, are stoichiometrically generated. NMR-scale polymerizations of propylene have been carried out by adding small amount of liquid propylene monomer to the NMR tube containing these cationic species dissolved in CD$_2$Cl$_2$ solvent. White *i*PP showing meso pentad value of over 84% is isolated in these polymerizations. Reacting *rac*-1 first with noncoordinating anion, and then methylating the resulting species leads to the decrease of yield to generate the cationic zirconium species. The coordinating anions such as $[HNMe_2Ph][BPh_4]$ and $[HNBu_3][BPh_4]$ are also less effective for the generation of methylzirconium cations than noncoordinating anions. The amount of MAO needed to activate *rac*-**1** can be decreased by methylating it with *2* equiv. of Al_2Me_6 before reacting with MAO.

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