In situ activation of *rac*-(SBI)Zr(NMe$_2$)$_2$ for the polymerization of propylene

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SUMMARY

Sequential NMR-scale reactions have been carried out in order to generate cationic methylzirconium complexes by the reaction of *rac*-(SBI)Zr(NMe$_2$)$_2$ (**1**, SBI = Me$_2$Si(indenyl)$_2$) with methylaluminoxane (MAO) or various noncoordinating anions such as [HNMePh$_2$] [B(C$_6$F$_5$)$_4$], [HNEt$_2$Ph][B(C$_6$F$_5$)$_4$], and [Ph$_3$C][B(C$_6$F$_5$)$_4$]. Reaction of 40 equiv. of MAO with **1** at room temperature was leaded to the formation of stable cationic methylzirconium complexes which polymerize propylene to isotactic polypropylene (iPP). For the activation of **1** with noncoordinating anions **1** was firstly methylated with 4 equiv. of AlMe$_3$ to give *rac*-(SBI)ZrMe$_2$ (**2**), and then 1 equiv. of noncoordinating anions was added to the resulting solution mixture containing **2** and various aluminum complexes dissolved in CD$_2$Cl$_2$ solvent. Complex **2** was immediately converted to cationic methylzirconium complex [*rac*-(SBI)Zr(μ-Me)$_2$AlMe$_2$]$^+$ (**3**), the adduct of the base-free *rac*-[(SBI)ZrMe]$^+$ cation and AlMe$_3$. Addition of small amount of liquid propylene to the NMR tube containing **3** and other byproducts was leaded to the formation of iPP showing meso pentad value of over 85 %.

INTRODUCTION

It is well established that cationic group 4 metal alkyl complexes of the type [Cp$_2$MR]$^+$ (M = Ti, Zr, Hf) are the active species in homogeneously catalyzed olefin polymerizations.[1] In conventional catalytic systems they are usually generated by the reaction of metallocene halides with an excess amount of MAO as activator. Alternatively, the reaction of dialkylmetallocenes with triphenylcarbenium or ammonium salts of weakly coordinating anions in nonbasic solvents leads quantitatively to cationic complexes, [Cp$_2$M-R]$^+$[B(C$_6$F$_5$)$_4$]$^-$ Coordinatively unsaturated cationic species [Cp$_2$M-R]$^+$ are potent electrophiles and may be expected to establish a series of solution equilibria by interaction with any neucleophile, such as the solvent, the anion, neutral metal alkyls, or the olefin substrate, prior to polymerization. During polymerization the neucleophile is removed to form base-free [Cp$_2$M-R]$^+$ or [Cp$_2$M(R)(olefin)]$^+$ species.[2-5] To synthesize the cationic species from Cp$_2$MX$_2$ excess amount of MAO is needed, so that it is difficult to study the procedure of formation of the active species. Alternatively alkylated metallocene complexes Cp$_2$MR$_2$ are needed to use noncoordinating anions as an activator.

Generally the yield to get Group 4 *ansa*-metallocene complexes which are highly effective for the stereospecific polymerization of α-olefin is low, and tedious isomer separation and purification steps are accompanied. Recently Jordan et al.[6] introduced new

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method to prepare racemic *ansa*-metallocene amide complexes selectively with a very high yield via an amine elimination route. In a previous study[6c] we have confirmed that the *ansa*-metallocene amide complexes could be directly activated for the polymerization of propylene by adopting various cocatalyst formulations. In this study we investigated the detailed activation procedures of *rac*-(SBI)Zr(NMe$_2$)$_2$ (**1**) based on NMR scale reactions with various cocatalysts such as MAO, [HNMePh$_2$][B(C$_6$F$_5$)$_4$] (**5**), [HNEt$_2$Ph][B(C$_6$F$_5$)$_4$] (**6**), and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (**7**). The activation procedures of conventional halide complex *rac*-(SBI)ZrCl$_2$ (**4**) were also investigated for the comparison.

EXPERIMENTAL

Materials   Polymerization grade of 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 **4** were synthesized according to previous procedures.[6] Various anionic complexes, **5**, **6**, and **7** were also prepared by literature procedures.[3,5,6]

Sequential NMR-scale reaction and polymerization   The procedure of in situ generating zirconium cationic species by the sequential reaction of **1**, AlMe$_3$, and **5** is exemplified below. **1** (20 mg, 42.9 μmol) was dissolved in CD$_2$Cl$_2$ (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 **1**. Addition of 4 equiv. of AlMe$_3$ was resulted in an orange solution representing complete methylation. After analyzing the solution mixture, **5** (37.0 mg, 42.9 μmol) was introduced into the NMR tube at room temperature to generate cationic zirconium complex. The color of solution mixture was immediately changed from orange to light yellow. After NMR analysis, about 0.1 - 0.5 mL of liquid propylene was added to the mixture at -78 °C, followed by slowly increased the temperature to room temperature. Solid iPP formed from the solution mixture 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$_6$D$_6$/1,2,4-trichlorobenzene (1/5) and were measured at 120 °C.

RESULTS AND DISCUSSION

To identify if ansa-metallocene diamide compounds could be activated by conventional procedures, we reacted **1** with MAO at room temperature by sequentially increasing the amount of MAO ([Al]/[**1**] = 10 to 40) in NMR-tube. Each solution mixture dissolved in CD$_2$Cl$_2$ was analyzed by ^{1}H NMR. Table 1 summarizes the chemical shifts of starting compounds and mixtures obtained by the reaction of **1** with MAO in different ratios ([Al]/[**1**] = 10, 20, and 40). The relative compositions obtained from the integration of each mixture are also indicated in Table 1. By sequentially increasing the amount of MAO from 10 to 40 equiv. after dissolving 20 mg (42.9 μmol) of **1** in 0,5 mL of CD$_2$Cl$_2$, NMe$_2$ ligands in **1** are firstly methylated by MAO and/or free AlMe$_3$ contained in MAO, followed by activated to give cationic active species. As shown in Table 1, **1**/10MAO mixture contains unreacted **1**, partially methylated compound (SBI)Zr(NMe$_2$)(Me) (**8**), completely methylated **2** and [(SBI)ZrMe]$^+$[MAO]$^-$ (**9**). The ratio of **1**/**8**/**2**/**9** is 1/2/1/1. Aluminum complex containing

Table 1. The Chemical Shifts of Various Compounds and Reaction Mixtures

Compounds or reaction mixtures	Identified compound	Relative composition	Chemical shifts (δ), identified (ppm)
5			8.8 (s, 1H), 7.64 (m, 6H), 7.41 (m, 4H), 3.83 (s, 3H)
7			8.27 (t, 3H), 7.87 (t, 6H), 7.66 (d, 6H)
MAO			Peaks were appeared at 3 characteristic regions as a broad multiplet: 4.0-3.4 (region 1), 1.4-1.7 (region 2), 1.2-0.6 (region 3). The integration ratio of region 1/region 2/region 3 was 2/3/20. Free Al_2Me_6 was appeared at -0.29 ppm as sharp singlet. Detailed interpretations of MAO were impossible.
1			7.68, 7.60 (d, 2H, indenyl), 7.05 (pseudo t, 2H, indenyl), 6.91 (d, 2H, C_5 indenyl), 6.79 (pseudo t, 2H, indenyl), 6.34 (d, 2H, C_5 indenyl), 2.37 (s, 12H, NMe_2), 1.05 (s, 6H, Si-Me)
Al_2Me_6			-0.29 (s)
1/AlMe₃	**1**	10	Chemical shifts are the same as above.
	8[1)]	15	7.76, 7.68[2)], 7.57 (d, 1H, indenyl), 7.19, 6.98, 6.86 (pseudo t, 1H, indenyl), 6.55, 6.46, 6.34[2)], 5.89 (d, 1H, C_5 indenyl), 2.28 (s, 6H, NMe_2), 1.06, 0.89 (s, 3H, Si-Me), -1.27 (s, 3H, Zr-Me)
	2	1	7.63[2)], 7.38 (d, 2H, indenyl), 7.26, 6.99[2)] (pseudo t, 2H, indenyl), 6.84[2)], 5.92 (d, 2H, C_5 indenyl), 0.91 (s, 6H, Si-Me), -1.43 (s, 6H, Zr-Me)
	10		2.42 (s, 6H, NMe_2), -0.54 (s, 15H, Al-Me)
	11		2.39 (s, 12H, NMe_2), -0.79 (s, 12H, Al-Me); The [**10**]/[**11**] ratio is 12/1.
1/2AlMe₃	**8**	2	7.76, 7.68 7.57[2)] (d, 1H, indenyl), 7.19, 6.98, 6.86[2)] (pseudo t, 1H, indenyl), 6.55, 6.46, 6.34, 5.89 (d, 1H, C_5 indenyl), 2.28, (s, 6H, NMe_2), 1.06, 0.89 (s, 3H, Si-Me), -1.27 (s, 3H, Zr-Me)
	2	3	7.63, 7.38[2)] (d, 2H, indenyl), 7.26, 6.99 (pseudo t, 2H, indenyl), 6.84, 5.92 (d, 2H, C_5 indenyl), 0.91 (s, 6H, Si-Me), -1.43 (s, 6H, Zr-Me)
	10, 11		The [**10**]/[**11**] ratio was measured to 7/1.
1/4 AlMe₃	**2**		7.63, 7.38 (d, 2H, indenyl), 7.26, 6.99 (pseudo t, 2H, indenyl), 6.84, 5.92 (d, 2H, C_5 indenyl), 0.91 (s, 6H, Si-Me), -1.43 (s, 6H, Zr-Me)
	10, 11		The [**10**]/[**11**] ratio was measured to 20/1.
1/4AlMe₃/**7**	**3**		7.77, 7.58 (d, 2H, indenyl), 7.08 - 7.34 (m, 4H, partially obscured by Ph_3CMe), 6.92, 5.93 (d, C_5 indenyl), 1.30 (s, 6H, Si-Me), - 0.78 (s, 6H, μ-CH_3), - 0.59 (s, 6H, Al-Me)
1/4AlMe₃/**5**	**3**		7.77, 7.58 (br d, 2H, indenyl), 7.00 - 7.38 (br m, 4H, partially obscured by NMe_2Ph), 6.92, 5.93 (br, 2H, C_5

			indenyl), 1.30 (s, 6H, Si-Me), - 0.79 (s, 6H, μ-CH₃), - 0.60 (s, 6H, Al-Me)
1/4AlMe₃/6	**3**		7.77, 7.58 (d, 2H, indenyl), 7.10 - 7.70 (br m, 6H, partially obscured by NEt₂Ph), 6.92, 5.93 (br d, 2H, C₅ indenyl), 1.30 (s, 6H, Si-Me), - 0.79 (s, 6H, μ-CH₃), - 0.60 (s, 6H, Al-Me)
1/10[MAO]	**1**	1	7.68[2)], 7.60 (d, 2H, indenyl), 7.05 (pseudo t, 2H, indenyl), 6.91 (d, 2H, C₅ indenyl), 6.79[2)] (pseudo t, 2H, indenyl), 6.34 (d, 2H, C₅ indenyl), 2.37 (s, 12H, NMe₂), 1.05 (s, 6H, Si-Me)
	8	2	7.76, 7.68[2)], 7.57[2)] (d, 1H, indenyl), 7.19[2)], 6.98[2)], 6.86[2)] (pseudo t, 1H, indenyl), 6.55, 6.46, 6.34[2)], 5.89 (d, 1H, C₅ indenyl), 2.28 (s, 6H, NMe₂), 1.06, 0.89 (s, 3H, Si-Me), - 1.27 (s, 3H, Zr-Me)
	2	1	7.63[2)], 7.38[2)] (d, 2H, indenyl), 7.26[2)], 6.99[2)] (pseudo t, 2H, indenyl), 6.84, 5.92 (d, 2H, C₅ indenyl), 0.91 (s, 6H, Si-Me), -1.43 (s, 6H, Zr-Me)
	9	1	7.85, 7.75 (d, 2H, indenyl), 7.50, 7.42[2)] (pseudo t, 2H, indenyl), 7.01[2)], 6.33 (d, 2H, C₅ indenyl), 1.20 (s, 6H, Si-Me), -0.63 (s, 3H, Zr-Me)
	11		2.38 (s, 12H, NMe₂), -0.79 (s, 12H, Al-CH₃)
	MAO		MAO could not be interpreted. Free AlMe₃ in MAO (- 0.29 ppm) was transformed into **11**.
1/20[MAO]	**2**	1	7.63, 7.38 (d, 2H, indenyl), 7.26, 6.99[2)] (pseudo t, 2H, indenyl), 6.84, 5.93 (d, 2H, C₅ indenyl), 0.91 (s, 6H, Si-Me), -1.43 (s, 6H, Zr-Me)
	9	1	7.85, 7.75 (d, 2H, indenyl), 7.50, 7.42[2)] (pseudo t, 2H, indenyl), 7.01, 6.33 (d, 2H, C₅ indenyl), 1.20 (s, 6H, Si-Me), -0.63 (s, 3H, Zr-Me)
	10, 11		The [**10**]/[**11**] ratio is measured to 3/1.
	MAO		MAO could not be interpreted. Free AlMe₃ in MAO was transformed into **10** and **11**.
1/40[MAO]	**9**		7.85, 7.75 (d, 2H, indenyl), 7.50, 7.42 (pseudo t, 2H, indenyl), 7.01, 6.33 (d, 2H, C₅ indenyl), 1.20 (s, 6H, Si-Me), -0.63 (s, 3H, Zr-Me)
	10, 11		The [**10**]/[**11**] ratio is measured to 2/1 and negligible amount of free AlMe₃ is observed.
	MAO		MAO could not be interpreted. Most of free AlMe₃ in MAO was transformed into **10** and **11**.

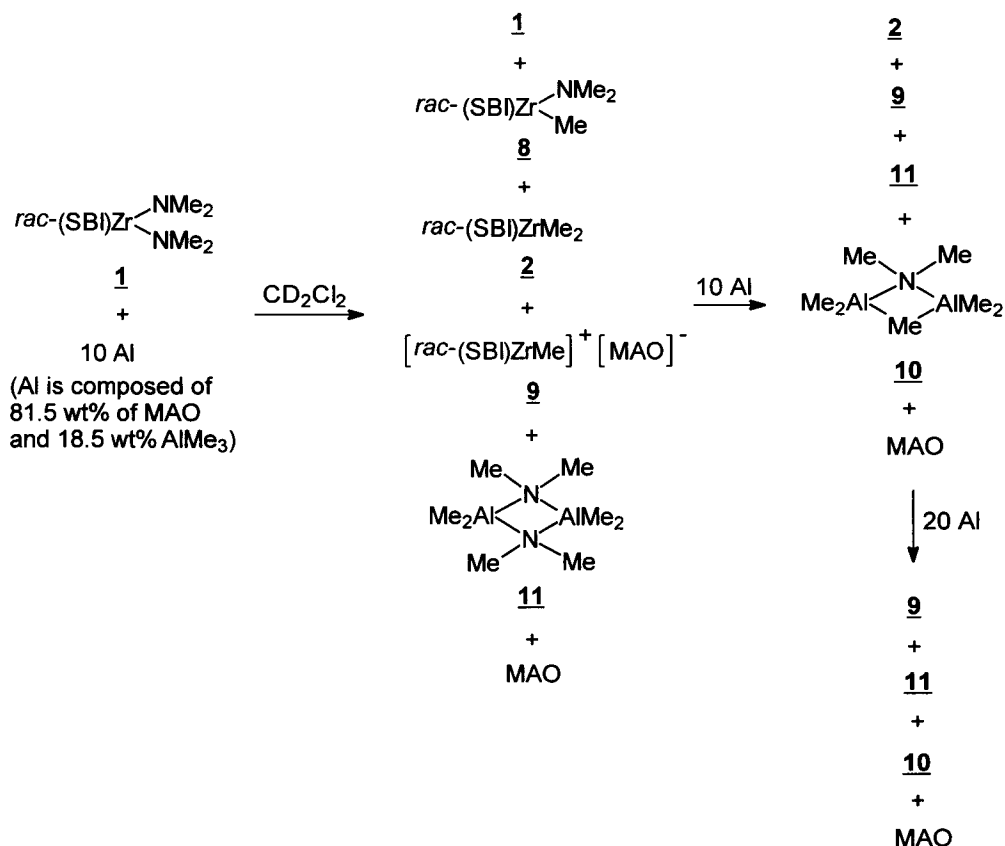[1)] Some chemical shifts could not be identified.

[2)] Partially obscured by the interference of other compounds in the solution mixture.

amine as a ligand, Al₂Me₄(NMe₂)₂ (**11**), is also observed. By sequentially adding 10 more equiv. of MAO ([Al]/[**1**] = 20) to the resulting mixture unreacted **1** and mixed alkyl compound **8** are completely disappeared to form **2** or **9**. The ratio of **2**/**9** is 1/1. Two kinds

of aluminum complexes, Al$_2$Me$_5$(NMe$_2$) (**10**) and **11**, are also observed. The ratio of **10/11** is 3/1. By further increasing the amount of MAO to [Al]/[**1**] = 40, **2** is completely activated to give cationic zirconium species **9**. The **10/11** ratio is changed to 2/1 in this mixture and only negligible amount of free Al$_2$Me$_6$ is observed. Since the 40 equiv. of Al is composed of 3.7 equiv. of Al originated from free Al$_2$Me$_6$ and 32.6 equiv. of Al from MAO, it is expected that most of free Al$_2$Me$_6$ contained in MAO is used for the methylation of **1**. Thus the methylation of **1** is seemed to be accomplished mainly by free AlMe$_3$. The methylation of **1** by AlMe$_3$ will be investigated later. The procedure for the formation of cationic zirconium species from the reaction of **1** with an excess amount of MAO can be summarized as shown in Scheme 1.

The methyl hydrogen peak representing **9** is recorded at -0.63 ppm in all mixtures of **1** and MAO. The structure of the cationic species and the nature of the interaction between MAO and zirconium cations under catalytic conditions employed here, in other words in CD$_2$Cl$_2$ solution, remain uncertain. However, the cationic species are very stable for a long time, i.e. the NMR signals of the solution mixture containing cationic species **9** was not changed for about a month at room temperature. In order to confirm the formation of active
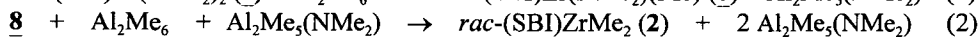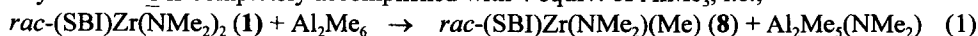
Scheme 1

1

+

rac- (SBI)Zr⟨NMe$_2$ / Me

8

+

rac-(SBI)ZrMe$_2$

2

+

[*rac-*(SBI)ZrMe]$^+$ [MAO]$^-$

9

+

Me∖ ∕Me

N

Me$_2$Al⟨ ⟩AlMe$_2$

N

Me∕ ∖Me

11

+

MAO

rac-(SBI)Zr⟨NMe$_2$ / NMe$_2$

1

+

10 Al

(Al is composed of 81.5 wt% of MAO and 18.5 wt% AlMe$_3$)

→ CD$_2$Cl$_2$ →

→ 10 Al →

2

+

9

+

11

+

Me∖ ∕Me

N

Me$_2$Al⟨ ⟩AlMe$_2$

Me

10

+

MAO

| 20 Al

↓

9

+

11

+

10

+

MAO

complex **9**, small amount of liquid propylene was introduced into the NMR tube containing the reaction mixture ([Al]/[**1**] = 40) at -78 °C. White iPP was precipitated from the solution mixture by slowly increasing the temperature of reaction mixture to room temperature. The meso pentad value (measured by ^{13}C NMR) of iPP isolated from the NMR tube was 85.2 %.

Analogous dichloride metallocene *rac*-(SBI)ZrCl$_2$ (**4**) could not be activated at the same reaction conditions. By reacting **4** with 40 equiv. of MAO in CD$_2$Cl$_2$ solution, methyl zirconocene compound **2** and cationic complex **9** were not observed at all. Small amount of mixed alkyl complex, *rac*-(SBI)Zr(Cl)(Me) was only recorded from the NMR signals. The methylation, followed by the activation was not accomplished even after increasing the reaction temperature to 70 °C for 12 hr. These results demonstrate that **4** is not easily methylated by the low concentration of MAO and/or free AlMe$_3$, thus difficult to give cationic complex **9**.

The methylation capability of metallocene diamide complex **1** was proved by the stoichiometrical reaction with AlMe$_3$ at room temperature. Table 1 summarizes the chemical shifts of solution mixtures obtained by the reaction of **1** with various amounts of AlMe$_3$ and their relative compositions. As the amount of AlMe$_3$ increases from [AlMe$_3$]/[**1**] = 1 to 4, dimethylzirconocene compound **2** was formed through intermediate compound **8**. The methylation of **1** is completely accomplished with 4 equiv. of AlMe$_3$, i.e.,
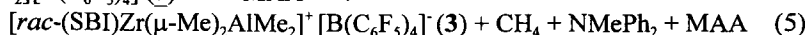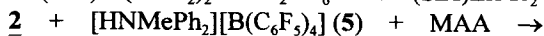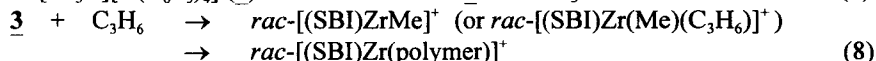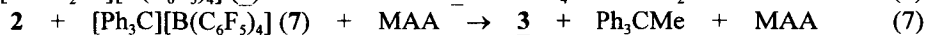
rac-(SBI)Zr(NMe$_2$)$_2$ (**1**) + Al$_2$Me$_6$ → rac-(SBI)Zr(NMe$_2$)(Me) (**8**) + Al$_2$Me$_5$(NMe$_2$) (1)

8 + Al$_2$Me$_6$ + Al$_2$Me$_5$(NMe$_2$) → rac-(SBI)ZrMe$_2$ (**2**) + 2 Al$_2$Me$_5$(NMe$_2$) (2)

Part of Al$_2$Me$_5$(NMe$_2$) is transformed into Al$_2$Me$_4$(NMe$_2$)$_2$,

2 Al$_2$Me$_5$(NMe$_2$) → Al$_2$Me$_6$ + Al$_2$Me$_4$(NMe$_2$)$_2$ (3)
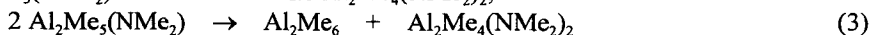
In the mixture of **1** with 4 equiv. of AlMe$_3$ three kinds of methylaluminum compounds, Al$_2$Me$_5$(NMe$_2$)/Al$_2$Me$_6$/Al$_2$Me$_4$(NMe$_2$)$_2$, were observed with the ratio of 20/1/1.

Since **1** is stoichiometrically methylated by AlMe$_3$, methylzirconium cations may be in situ generated by adding non-coordinating anions such as **5**, **6**, and **7** to AlMe$_3$/**1** (4/1) mixture. As shown in Table 1, addition of 1 equiv. of [HNMePh$_2$][B(C$_6$F$_5$)$_4$] (**5**), [HNEt$_2$Ph][B(C$_6$F$_5$)$_4$] (**6**), or [Ph$_3$C][B(C$_6$F$_5$)$_4$] (**7**) to the solution mixture of AlMe$_3$/**1** (4/1) resulted in immediate conversion to [*rac*-(SBI)Zr(μ-Me)$_2$AlMe$_2$]$^+$ (**3**), the adduct of the base-free *rac*-[(SBI)ZrMe]$^+$ cation and AlMe$_3$ which was previously identified by Bochmann[18] as the principal component in mixtures of these species. Bochmann has synthesized the cationic compound **3** by reacting *rac*-(SBI)ZrMe$_2$ with **7** at low temperature (- 40 °C). In our study the same cationic species **3** have been generated regardless of the type of anions. However, in the case of **5** and **6**, the resonance of **3** and the Al amide species are broadened. Complex **3** presumably undergoes loss or displacement of AlMe$_3$ during polymerization, ultimately leading to *rac*-[(SBI)ZrMe]$^+$ or *rac*-[(SBI)Zr(Me)(propene)]$^+$ species. To confirm this fact liquid propylene was added to the mixture, **1**/AlMe$_3$/non-coordinating anion (1/4/1), at - 78 °C, and then slowly increased the temperature to room temperature. White iPP was precipitated in this process. The meso pentad value of iPP precipitated by adding liquid propylene to the mixture of **1**/4AlMe$_3$/**5**, **1**/4AlMe$_3$/**6**, and **1**/4AlMe$_3$/ **7** was 88.7 %, 86.4 %, and 87.7 %, respectively. The formation of base-free methyl-zirconium cations by non-coordinating anions can be summarized as follows,

rac-(SBI)Zr(NMe$_2$)$_2$ + 2Al$_2$Me$_6$ → rac-(SBI)ZrMe$_2$ (**2**) + methylaluminum amides (MAA) (4)

2 + [HNMePh$_2$][B(C$_6$F$_5$)$_4$] (**5**) + MAA →

[*rac*-(SBI)Zr(μ-Me)$_2$AlMe$_2$]$^+$ [B(C$_6$F$_5$)$_4$]$^-$ (**3**) + CH$_4$ + NMePh$_2$ + MAA (5)

$$\underline{2} + [HNEt_2Ph][B(C_6F_5)_4] \ (\underline{6}) \quad + \quad MAA \rightarrow \quad \underline{3} \quad + \quad CH_4 \quad + \quad NEt_2Ph \quad + \quad MAA \qquad (6)$$

$$\underline{2} \quad + \quad [Ph_3C][B(C_6F_5)_4] \ (\underline{7}) \quad + \quad MAA \quad \rightarrow \quad \underline{3} \quad + \quad Ph_3CMe \quad + \quad MAA \qquad (7)$$

$$\underline{3} \quad + \quad C_3H_6 \quad \rightarrow \quad rac\text{-}[(SBI)ZrMe]^+ \quad (or \ rac\text{-}[(SBI)Zr(Me)(C_3H_6)]^+ \ )$$

$$\rightarrow \quad rac\text{-}[(SBI)Zr(polymer)]^+ \qquad (8)$$
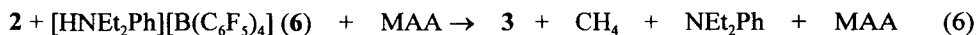
The solution mixture containing cationic complex $\underline{3}$ is stable, so that the mixture is not decomposed after storing for about a month at room temperature and even after heating to 70 °C for 12 hours. On cooling to - 20 °C $\underline{3}$ precipitates as an oil which could not be crystallized. The structure of $\underline{3}$ in solution is assumed to be different from that of cationic species $\underline{9}$ generated using MAO as an anion. As shown in Table 1, the chemical shift of Zr-Me in $\underline{3}$ which has 6 hydrogens is - 0.78 ppm, on the other hand that of $\underline{9}$ which has 3 hydrogens is - 0.63 ppm.

As a conclusion *ansa*-metallocene amide derivative $\underline{1}$, which is efficiently prepared via an amine elimination route, can be used directly in catalyst formulation for the olefin polymerization. In addition the simplicity of the alkylation reaction of $\underline{1}$ proves advantageous in studies of the solution structure and reactivity of MAO. More thorough studies of the influence of the nature and concentration of the AlR_3 reagent and the polymerization conditions on the catalyst performance and polymer properties are in progress.

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