Preparation of $Al(C_6F_5)_3$ and its use for the modification of methylalumoxane

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Abstract

Tris(pentafluorophenyl)aluminum was prepared from a metathesis between $AlMe_3$ and $B(C_6F_5)_3$ in a quantitative yield. Out of CN stretching frequency of various benzonitrile adducts, it is found that the title aluminum compound is a quite weaker Lewis acid than $B(C_6F_5)_3$ is, and has rather similar acidity as $AlMe_3$. When mixtures of methylalumoxane (MAO) and $Al(C_6F_5)_3 \cdot (toluene)_{0.5}$ or $B(C_6F_5)_3$ were heated at 65°C, it is observed that the C_6F_5 group was exchanged with the methyl group of the MAO. Several MAOs were prepared with variable degrees of modification. Catalytic activity of pristine MAO and modified MAOs were tested for ethylene and propylene polymerization. It is found that the activity is enhanced with the modification, and the effectiveness is reduced as modification level is increased. In particular, 7-fold increase of activity for polyethylene is observed, when 5.5×10^{-3} equimolar amount of $Al(C_6F_5)_3 \cdot (toluene)_{0.5}$ is used for the modification. The modification with $B(C_6F_5)_3$ incorporates boron atoms into the oligomeric chain, and is less effective than that with the aluminum analogue. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the reports of Sinn and Kaminsky [1], Sinn et al. [2] and Pasynkiewicz [3], methylalumoxane (MAO) has been widely used as a co-catalyst for Ziegler–Natta type polymerization [4–8]. Due to its superb activity the aluminum catalyst has been a topic of intense research in the academic and industrial domains [9–19]. Moreover, recent advances in homogeneous catalysts for the alkene polymerization highlight its importance [4,20–23].

Because of its inherent structural complexity MAO has escaped full characterization. Only recently, its structure could be deduced from crystal structures of *tert*-butyl-substituted alumoxanes [24],

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spectroscopic data [25], and other analytical methods [26]. Also it is known that preparative methods determine its molecular weight and structure, eventually catalytic activity [13–19].

Effect of other substituents on the aluminum center has not been reported. Choice of the substituents is very limited because the pendant group should be noncoordinating to the strongly electrophilic metallic center in which a polymeric chain grows, otherwise the activity for the polymerization is hampered.

Weakly coordinating $B(C_6F_5)_4$-anion [27–33] stimulates the use of C_6F_5 group for the modification of MAO. Herein, we wish to report facile synthesis of $Al(C_6F_5)_3 \cdot (toluene)_{0.5}$ from $B(C_6F_5)_3$, and modification of MAO with both aluminum and boron reagents.

2. Experimental

2.1. General

All manipulation of air- and/or moisture-sensitive compounds was carried out with use of standard Schlenk or vacuum-line technique. Argon was purified by passage through columns of Ridox oxygen scavenger (R31-3, Fisher) and Linde 4-Å molecular sieves. Solids were transferred and stored in an N_2-filled Vacuum Atmospheres glovebox equipped with a HE-493 Dri-Train, a CS-40 Dri-Cold, and an oxygen analyzer (Model 315, Teledyne Analytical Instruments).

Benzene was stirred over CaH_2 and then transferred to a sodium/benzophenone ketyl. Anhydrous toluene, tetrahydrofuran, and diethyl ether were purchased from Aldrich, and transferred to a sodium/benzophenone ketyl without prior treatment. Pentane was stirred over concentrated H_2SO_4, dried over CaH_2, and then transferred to a sodium/benzophenone ketyl. Dichloromethane was dried over CaH_2 and degassed by evacuation using freeze–pump–thaw cycles. Dried deoxygenated solvents were vacuum-transferred to dry glass vessels equipped with a J-young valve and stored under argon. Benzene-d_6 and toluene-d_8 were vacuum-transferred from purple sodium/benzophenone ketyl. Benzonitrile was dried over anhydrous $MgSO_4$, and then vacuum-distilled to a dry glass vessel, stored over Linde 4-Å molecular sieves, and finally degassed through freeze–pump–thaw cycles. $AlMe_3$ (97%, Aldrich), n-BuLi (1.6 M in hexane, Aldrich), BCl_3 (1.0 M in hexane, Aldrich), $MgCl_2 \cdot 6H_2O$ (99%, Aldrich), and C_6F_5Br (>99%, Tokyo Kasei Kogyo) were used as purchased. $B(C_6F_5)_3$ [32] and MAO [13] were prepared as in the literatures. Ethylene (polymer grade) was purchased from Matheson Gas Products, and used after passing through columns packed with Ridox oxygen scavenger and Linde 4-Å molecular sieves.

NMR spectra were recorded on a Bruker DPX300 (300 MHz, ^{1}H; 121 MHz, ^{13}C) spectrometer. Chemical shifts are reported in δ, referenced to residual solvent signals. $^{19}F\{^1H\}$ NMR and $^{11}B\{^1H\}$ NMR data are referenced externally to CF_3COOH and $B(OH)_3$ dissolved in D_2O, respectively (downfield positive). IR spectra were recorded on an evacuable Bomem DA8 FT-IR spectrophotometer. Spectra were taken while a sample chamber was evacuated in order to eliminate CO_2 interference. Molecular weights of the alumoxanes were measured by isothermal distillation method [34]. A polystyrene of known molecular weight (MW = 2500, Aldrich) was used as the standard. Elemental analyses were performed at Galbraith Laboratory.

2.2. Preparation of tris(pentafluorophenyl)aluminum $\cdot$ (toluene)$_{0.5}$

When $AlMe_3$ (0.020 ml, 0.21 mmol) was added to sublimed $B(C_6F_5)_3$ (106 mg, 0.207 mmol) dissolved in toluene (3 ml) at room temperature, bubbles were observed. The solution was stirred for

1 h, and drying in vacuo produced a white solid (126 mg, 0.203 mmol, 98%). ^{19}F NMR (C_6D_6) δ −46.4 (d, 6F, *ortho*), −74.1 (t, 3F, *para*), −83.9 (t, 6F, *meta*); ^{1}H NMR (C_6D_6) δ 7.07 (m, 5H), 2.09 (s, 3H). Calcd. for $C_{18}AlF_{15}(C_7H_8)_{0.5}$: C, 44.97; H, 0.70. Found: C, 44.52; H, 1.00. For recrystallization, the solid (30 mg) was dissolved in THF (0.5 ml), and hexane (5 ml) was layered on the top of the solution. After 2 or 3 days, the solution produced transparent white crystals, $Al(C_6F_5)_3 \cdot$ THF, suitable for elemental analysis: ^{19}F NMR (C_6D_6) δ −46.4 (d, 6F, *ortho*), −74.5 (t, 3F, *para*), −84.1 (t, 6F, *meta*); ^{1}H NMR (C_6D_6) δ 3.42 (t, 4H), 1.00 (t, 4H); Anal. Calcd. for $C_{22}H_8AlF_{15}O$: C, 44.02; H, 1.34. Found: C, 43.52; H, 1.29.

2.3. Preparation of benzonitrile adducts of $AlMe_3$, $Al(C_6F_5)_3$, and $B(C_6F_5)_3$

The aluminum and the boron reagents were added in benzene, dissolving an equimolar amount of benzonitrile, and the mixtures were stirred for 2 h at room temperature. The solid benzonitrile adducts were obtained by evaporating the solution in vacuo. IR spectra of the solids were recorded right after the KBr pellets were made in the glove box.

2.4. Preparation of methylalumoxane

$MgCl_2 \cdot 6H_2O$ (3.00 g, 14.8 mmol) in toluene (8 ml) was added to a 100-ml flask equipped with a magnetic stirrer, a nitrogen inlet and a dropping funnel [13]. The suspension was cooled to 0°C, then $AlMe_3$ (4.70 ml, 49.3 mmol) in toluene (20 ml) was added dropwise at 0°C for 1 h. Then, the reaction mixture was gradually heated up to 50°C and stirred at this temperature for 24 h. After filtration, the solid-like MAO (0.84 g, $Y = 29\%$) was obtained by evaporating the filtrate to dryness: ^{1}H NMR (toluene-d_8) δ −0.01 (br), −0.15 (s); ^{13}C NMR (toluene-d_8) δ −6.98 (br). ^{1}H NMR spectrum shows a broad resonance as well as a sharp resonance, where the latter is attributed to bound $AlMe_3$ to the MAO through a chemical association. Molecular weight of the oligomer was measured to be 2.1×10^3 from the isothermal distillation.

2.5. Modification of methylalumoxane with $B(C_6F_5)_3$

Sublimed $B(C_6F_5)_3$ [32] (11.6 mg for MMAO-1) was added to the above MAO (250 mg) dissolved in toluene (10 ml) at room temperature. The solution was gradually heated up to 60–65°C and stirred for 12 h at the temperature. After the solution was cooled to room temperature, glassy residue was obtained by evaporating in vacuo ($Y > 80\%$): ^{1}H NMR (toluene-d_8) δ 0.06 (br). For ^{19}F NMR spectra, the reactants (28 mg of MAO, 25 mg of $B(C_6F_5)_3$) were added in an NMR tube, subsequently toluene-d_8 (0.5 ml) was vacuum-transferred, and finally the tube was flame-sealed to keep volatile products from escape. After the NMR tube was heated at 65°C for 12 h, ^{19}F and ^{11}B NMR spectra were recorded. ^{19}F NMR (toluene-d_8) δ −49.7 (br, *ortho*), −77.7 (br, *para*), −86.6 (br, *meta*). ^{11}B NMR (toluene-d_8): d 72.3 (s). When the sample was rigorously evacuated to dryness and redissolved in toluene-d_8, no ^{11}B resonance was observed at all. The dried sample was analyzed. Anal. Found: C, 30.13; H, 1.74; Al, 23.03; B: 0.20.

2.6. Modification of methylalumoxane with $Al(C_6F_5)_3 \cdot (toluene)_{0.5}$

Certain amount of $Al(C_6F_5)_3 \cdot (toluene)_{0.5}$ (13.5 mg for MMAO-2; 26.7 mg for MMAO-3; 53.4 mg for MMAO-4) was added to the above MAO (250 mg, ca. 4.3 mmol of Al) dissolved in toluene (10

ml) at room temperature. The solution was gradually heated up to 60–65°C and stirred for 12 h. After the solution was cooled to room temperature, glassy residue was obtained by evaporating in vacuo ($Y > 80\%$): ^{1}H NMR (toluene-d_8) δ 0.04 (br); Only broad peaks are observed in ^{19}F NMR spectroscopy. ^{19}F NMR (toluene-d_8) δ -48.5 (br, *ortho*), -78.3 (br, *para*), -86.9 (br, *meta*).

2.7. Polymerization of ethylene

Out of toluene solution (20 ml) dissolving zirconocene dichloride (2.0 mg), 1.0 ml of the solution was taken, and it was transferred in a 500 ml heavy-wall glass pressure reactor. A MAO was weighed to adjust the molar ratio of aluminum to zirconium to 1600:1. Together with the measured MAO, 10% trimethylaluminum in toluene (1.0 ml) and 250 ml of toluene were added in the reactor. The resulting solution was stirred at 80°C under 40 psi of ethylene for 15 min. The polymerization was quenched by evacuation of ethylene and subsequent addition of ethanolic solution (300 ml) of HCl. White precipitate was filtered and washed with copious ethanol, and finally dried in a vacuum oven at 60°C for 12 h.

2.8. Polymerization of propylene

Out of toluene solution (20 ml) dissolving *rac*-(1,2-ethylenebis(η^5-indenyl))zirconium dichloride (5.0 mg), 2.0 ml of the solution was taken, and it was transferred in a 500 ml heavy-wall glass pressure reactor. Each MAO was weighed to adjust the molar ratio of aluminum to zirconium to 1600:1. Together with the measured MAO, 10% trimethylaluminum in toluene (1.0 ml) and 250 ml of toluene were added in the reactor. The resulting solution was stirred at 80°C under 40 psi of propylene for 1 h. The polymerization was quenched by evacuation of propylene and subsequent addition of methanolic solution of HCl. After toluene was evaporated to reduce its volume to about 100 ml, acetone was added to produce a white precipitate. The precipitate was filtered, and washed with copious methanol and subsequently copious acetone, and finally dried in a vacuum oven at 60°C for 12 h.

3. Results and discussion

3.1. Synthesis of Al(C$_6$F$_5$)$_3$ · solvent

Preparation of Al(C$_6$F$_5$)$_3$ · diethyl ether and Al(C$_6$F$_5$)$_3$ · THF has been reported previously [35,36]. These compounds were heated under vacuum in order to eliminate the oxygen-containing solvents from the Lewis acidic center, but the THF adduct only decomposed at elevated temperatures (> 200°C). Special care was taken for the heating because there are reports that Al(C$_6$F$_5$)$_3$ and/or its adducts are explosive [36,37].

It was observed that as soon as trimethylaluminum(l) was contacted with solvent-free B(C$_6$F$_5$)$_3$, bubbles, later identified as BMe$_3$ (boiling point $= -20$°C), were formed. ^{19}F NMR spectrum of residual solid showed that new resonances were very similar to those of Al(C$_6$F$_5$)$_3$ · THF (Eq. (1)). When toluene was used as a solvent for the better mixing, only a Al(C$_6$F$_5$)$_3$ · (C$_7$H$_8$)$_{0.5}$ was detected after evaporating the reaction mixture in vacuo (Eq. (2)). Presence of toluene is obvious from ^{1}H NMR spectrum, and the stoichiometry of toluene has been determined as 0.50 from elemental analysis. The product is pure enough to use it without further purification steps. No necessity to use

Table 1
Stretching frequency of CN bond of benzonitrile and benzonitrile acid adducts

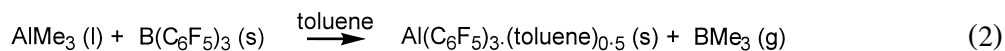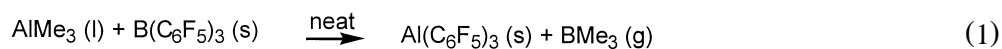| Compounds	ν(CN) (cm^{-1})[a]	Difference (cm^{-1})
PhCN	2230	
PhCN · AlMe$_3$	2276 (this work), 2271[b]	46 (this work), 41[b]
PhCN · Al(C$_6$F$_5$)$_3$	2280	50
PhCN · B(C$_6$F$_5$)$_3$	2324	94

[a]As KBr pellets, except benzonitrile.
[b]Ref. [38].

oxygen-containing solvents is one of advantages of the metathesis. Also, in our laboratory, impure solvent-free Al(C$_6$F$_5$)$_3$, purified Al(C$_6$F$_5$)$_3$ · (toluene)$_{0.5}$, and Al(C$_6$F$_5$)$_3$ · THF have been heated up to 200°C under nitrogen for the test. However, no incidence of explosion has been met in our laboratory.

It is interesting to notice that trimethylaluminum gives a clean metathesis, but triethylaluminum does not. Pohlmann and Brinckmann [36] reported that B(C$_6$F$_5$)$_3$ and the latter aluminum reagent gave only tarry products at 50°C, and even detonated when heated to 70°C. Out of NMR analysis we found that the reaction with triethylaluminum produces the Al(C$_6$F$_5$)$_3$ along with numerous side products at room temperature. Obviously, volatility of trimethylboron helps to drive the reaction complete.

The product is soluble in benzene, toluene, and other hydrocarbon solvents, and too soluble to be recrystallized in these solvents. The product was dissolved in a minimum amount of THF, and hexane was layered on the top of the THF solution. In several days, white crystals of which spectral data are exactly same as those of Al(C$_6$F$_5$)$_3$ · THF were obtained [35]. [1]

$$AlMe_3 \text{ (l)} + B(C_6F_5)_3 \text{ (s)} \xrightarrow{\text{neat}} Al(C_6F_5)_3 \text{ (s)} + BMe_3 \text{ (g)} \tag{1}$$

$$AlMe_3 \text{ (l)} + B(C_6F_5)_3 \text{ (s)} \xrightarrow{\text{toluene}} Al(C_6F_5)_3 \cdot (toluene)_{0.5} \text{ (s)} + BMe_3 \text{ (g)} \tag{2}$$

3.2. Lewis acidity of AlMe$_3$, Al(C$_6$F$_5$)$_3$, and B(C$_6$F$_5$)$_3$

Lewis acidity of the aluminum and the boron reagents was measured. It is known that stretching frequency of CN bond of benzonitrile acid adduct is dependent on strength of Lewis acids [38]. The stronger a Lewis acid is, the higher stretching frequency of the benzonitrile acid adduct is observed. As can be seen in Table 1, Al(C$_6$F$_5$)$_3$ adducts absorb at slightly higher frequency than AlMe$_3$, but B(C$_6$F$_5$)$_3$ adduct resonates at much higher frequency than those two aluminum adducts. The spectroscopic result clearly shows that the boron reagent is the stronger Lewis acid than the other two aluminum reagents, and the pentafluorophenyl substituent is only marginally effective to increase Lewis acidity.

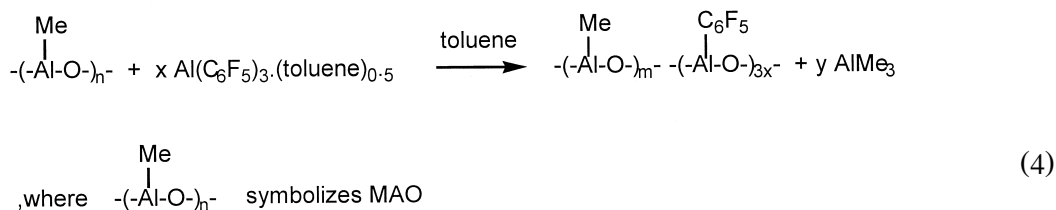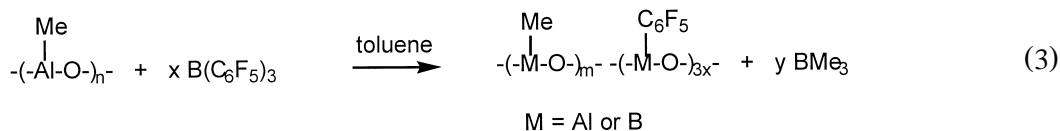[1] Converted chemical shifts (-123.4, -151.5, -161.1 ppm) in reference to CFCl$_3$ are in accord with the reported values.

3.3. Preparation of modified MAO

Facile metathesis between $AlMe_3$ and $B(C_6F_5)_3$ implied that the methyl group of MAO can be easily exchanged by C_6F_5 group of $B(C_6F_5)_3$, even of $Al(C_6F_5)_3$. While Michiels and Muñoz-Escalona [39] observed the enhanced reactivity of MAO when $B(C_6F_5)_3$ was used as an additive, the overlooked metathesis could be associated with the modulation of the activity. The process is economical because it does not lose precious C_6F_5 group. Significant portion of the group will be lost as C_6F_5H if a mixture of $AlMe_3$ and $Al(C_6F_5)_3$ or $B(C_6F_5)_3$ was hydrolyzed to form modified MAO.

When $B(C_6F_5)_3$ was mixed with the above prepared MAO in toluene-d_8 and heated, it was indeed found that there was a facile exchange. After heating, only broad resonances in ^{19}F NMR spectroscopy were observed, and concurrent generation of a single sharp peak of BMe_3 was observed in ^{11}B NMR spectroscopy [40]. The ^{19}F NMR spectrum is very similar to that of MAO modified with $Al(C_6F_5)_3$ (vide infra). After evaporating the sample, the [11]B resonance is totally disappeared. However, elemental analysis of the dried sample showed that most of boron was remained in the oligomeric chain. Therefore, it can be said that only small part of boron reagent transformed into volatile BMe_3, but most of boron is incorporated into the oligomeric chain (Eq. (3)). Also, most of C_6F_5 group are bound to the aluminum center rather than the boron center, presumably due to statistical reason.

When $Al(C_6F_5)_3 \cdot (toluene)_{0.5}$ is mixed with the MAO in toluene-d_8 and heated, broad resonances were appeared, and no sharp resonance attributed to $Al(C_6F_5)_3$ is remained in ^{19}F NMR spectroscopy. The positions of the broad resonances are exactly same as for the $B(C_6F_5)_3$ case. The spectroscopic data support that there is a complete metathesis to generate $AlMe_3$ together with modified MAO (Eq. (4)).

Because all of MAO contains variable amount of $AlMe_3$, there is also possibility that both boron and aluminum reagents metathesize with the trimethylaluminum concurrently. However, the fact that major portion of C_6F_5 group is incorporated into the MAO is evident from the broadening of ^{19}F NMR spectra. Also, very similar ^{19}F NMR spectrum has been obtained from the direct partial hydrolysis of $Al(C_6F_5)_3$.

$$\underset{\underset{\text{-(-Al-O-)}_n\text{-}}{|}}{\overset{\text{Me}}{}} + x\,B(C_6F_5)_3 \xrightarrow{\text{toluene}} \underset{\underset{\text{-(-M-O-)}_m\text{- -(-M-O-)}_{3x}\text{-}}{|\quad\quad|}}{\overset{\text{Me}\quad\quad C_6F_5}{}} + y\,BMe_3 \qquad (3)$$

$$M = Al \text{ or } B$$

$$\underset{\underset{\text{-(-Al-O-)}_n\text{-}}{|}}{\overset{\text{Me}}{}} + x\,Al(C_6F_5)_3\cdot(toluene)_{0.5} \xrightarrow{\text{toluene}} \underset{\underset{\text{-(-Al-O-)}_m\text{- -(-Al-O-)}_{3x}\text{-}}{|\quad\quad|}}{\overset{\text{Me}\quad\quad C_6F_5}{}} + y\,AlMe_3$$

$$(4)$$

$$\text{,where }\underset{\underset{\text{-(-Al-O-)}_n\text{-}}{|}}{\overset{\text{Me}}{}}\text{ symbolizes MAO}$$

3.4. Catalytic activity for ethylene polymerization

Catalytic activity of pristine MAO and modified MAOs are tested in the presence of Cp_2ZrCl_2 in toluene. Ratio of Cp_2ZrCl_2 and MAO was maintained at 1:1600 (mol of Zr vs. Al) and is not optimized. As can be seen in Table 2, the catalytic activity is increased significantly by substituting

Table 2
Catalytic activity of pristine MAO and modified MAOs for ethylene polymerization

Co-catalyst	Molar ratio ([MeAlO]: $Al(C_6F_5)_3 \cdot (toluene)_{0.5}$)	Activity[a] (kg PE/g cat h)
pristine MAO[b]	–	39
MMAO-1[c]	100:0.50	144
MMAO-2	100:0.55	272
MMAO-3	100:1.1	176
MMAO-4	100:2.2	110

[a] The activity was measured under 40 psi of ethylene at 80°C. Weights of the polyethylene was extrapolated from those obtained at 15 min of the reaction.
[b] For comparison the MAO was heated at 65°C for 12 h without addition of the aluminum or the boron reagents.
[c] $B(C_6F_5)_3$ is used for the case.

Table 3
Catalytic activity of MMAO-2 at various Al/Zr ratios for ethylene polymerization[a]

Co-catalyst	$Al/Zr^b = 1600$	$Al/Zr = 400$	$Al/Zr = 100$
MMAO-2	272	95	18

[a] The activity was measured under 40 psi of ethylene at 80°C. Weights of the polyethylene was extrapolated from those obtained at 15 min of the reaction. Units are in kg PE/g cat h.
[b] Al/Zr represents the molar ratio of aluminum center of MMAO-2 to zirconocene dichloride.

some of the methyl group with C_6F_5 group. Modification with $B(C_6F_5)_6$ increases the activity by 3.7-fold. With $Al(C_6F_5)_3 \cdot (toluene)_{0.5}$, further increase of the activity up to 7-times is achieved. However, heavier substitution reduces the favorable effect of the fluorinated phenyl group.

While the sizable increase of the catalytic activity was observed for MMAO-2, the amount of MMAO-2 was varied to elucidate its influence to the activity. As in Table 3, the molar ratio of aluminum center of MMAO-2 to zirconocene dichloride has been reduced from 1600 to 400 and 100. With the constant amount of trimethylaluminum as a scavenger, the activity changes from 272 kg PE/g cat h to 95 kg PE/g cat h, and it decreases finally to 18 kg PE/g cat h. Therefore, as for the pristine MAO, the amount of the employed modified MAO greatly affects the catalytic activity.

It can be speculated that the new aluminum center having the noncoordinating substituent, i.e., pentafluorophenyl group is more effective for the abstraction of a methyl group from zirconocene. Alternatively the new center increases the reactivity due to the reduced association between the cationic catalytic center and the counter-ion. For the cases, thermodynamic favor of the new center over the methyl aluminum center should be assumed (Scheme 1), because the enhanced reactivity is evident even with the modification of the low extent. Also, the heavier modification of MAO as well as the incorporation of boron atom could alter the desirable original structure, and the alterations must result in the reduction of the effectiveness.

3.5. Catalytic activity for propylene polymerization

Catalytic activity of pristine MAO and modified MAOs are tested in the presence of *rac*-(1,2-ethylenebis(η^5-indenyl))ZrCl$_2$ in toluene. Ratio of *rac*-(EBI)ZrCl$_2$ and MAO was maintained at 1:1600
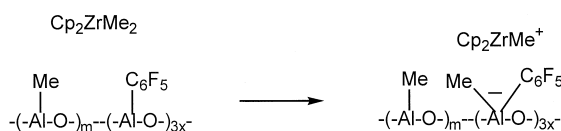
Scheme 1.

Table 4
Catalytic activity of pristine MAO and modified MAOs for propylene polymerization

Co-catalyst	Molar ratio ([MeAlO]: $Al(C_6F_5)_3 \cdot (toluene)_{0.5}$)	Activity[a] (kg PP/g cat h)
pristine MAO[b]	–	20
MMAO-2	100:0.55	26
MMAO-3	100:1.1	13
MMAO-4	100:2.2	10

[a]The polymerization was carried out under 40 psi of propylene at 80°C for 1 h using *rac*-(EBI)ZrCl$_2$ (Al/Zr = 1600).
[b]For comparison the MAO was heated at 65°C for 12 h without addition of the aluminum reagent.

(mol of Zr vs. Al) as in the polymerization of ethylene. As in Table 4, the catalytic activity is modulated by substituting some of the methyl group of MAO with C_6F_5 group. The most effective MAO for ethylene polymerization, that is, MMAO-2 produces the highest yield of polypropylene. Therefore, the effectiveness of the substitution with C_6F_5 group is evident for both polymerizations, even though the effectiveness is so reduced that only marginal increase of the activity (30%) is observed for propylene polymerization. Rather highly modified MAOs such as MMAO-3 and MMAO-4 produce lower weight of polypropylene than that for the pristine MAO. The last undesirable effect with the high modification is also observed for ethylene polymerization.

4. Conclusion

A facile metathesis between $AlMe_3$ and $B(C_6F_5)_3$ produces tris(pentafluorophenyl)aluminum in a quantitative yield. Thermal exchange between the methyl group of MAO and the pentafluorophenyl group of both $B(C_6F_5)_3$ and $Al(C_6F_5)_3$ was observed. The modification of MAO with the noncoordinating group modulates the catalytic reactivity for the olefin polymerization.

Acknowledgements

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