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Ethylene Polymerization by Phenoxy Substituted Tris(pyrazolyl)borate Ti(IV) Methyl Complexes

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ABSTRACT: Ethylene polymerization using Tp*TiMe$_2$(OAr) [Tp* = HB(3,5-Me$_2$-pyrazolyl)$_3$; Ar = O-2, 6-Me$_2$C$_6$H$_3$ (**2a**), O-2,6-^{i}Pr$_2$C$_6$H$_3$ (**2b**)]-cocatalyst systems [cocatalyst: MAO, [Ph$_3$C][B(C$_6$F$_5$)$_4$], or B(C$_6$F$_5$)$_3$ and Al^{i}Bu$_3$ or Al(n-octyl)$_3$] or[Tp*TiMe(O-2,6-Me$_2$C$_6$H$_3$)]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$·2THF (**3a**) in the presence of Al alkyls have been explored. The catalytic activity by **2a**,**b**−cocatalyst systems was highly affected by the Al/Ti molar ratios. Ethylene polymerizations by **2a**,**b**−MAO catalyst systems proceeded in a quasi living manner between −30 and 25 °C, whereas certain degree of chain transfer was observed when the polymerizations by **2a**,**b** were conducted in the presence of borate cocatalysts. The activity by the cationic Ti(IV)−methyl complex (**3a**) in the presence of Al(n-octyl)$_3$ was close to those by **2a**−B(C$_6$F$_5$)$_3$−Al(n-octyl)$_3$, Al^{i}Bu$_3$ catalyst systems and the M_n values in the resultant polymers were close with uniform distributions; the facts clearly indicate that the same catalytically active species play a role in this catalysis.

Introduction

Design of efficient molecular catalysts for precise olefin polymerization attracts considerable attention in the field of organometallic chemistry, catalysis, and of polymer chemistry.[1−6] Half-titanocenes containing anionic donor ligands of type Cp′TiX$_2$(Y) (Cp′ = cyclopentadienyl group; X = halogen, alkyl; Y = aryloxo, ketimide, phosphinimide, etc.) are promising candidates,[5] especially in terms of syntheses of new polymers by ethylene copolymerizations as demonstrated by using the aryloxo and the ketimide analogues.[5b,7] Tris(pyrazolyl)borate group 4 metal complexes, Tp′MCl$_3$ [Tp′ = tris(pyrazolyl)borate; M = Ti, Zr, Hf], are known to exhibit high catalytic activities for ethylene polymerization in the presence of methylalumoxane (MAO),[8−11] and that the cationic species, generated in situ from Tp*Zr(CH$_2$Ph)$_3$ [Tp* = HB(3,5-Me$_2$-pyrazolyl)$_3$] or Tp^{Ms*}Hf(CH$_2$Ph)$_3$ [Tp^{Ms*} = HB(3-mesitylpyrazolyl)$_2$(5-mesitylpyrazolyl)$^-$] and [Ph$_3$C][B(C$_6$F$_5$)$_4$], polymerize ethylene.[12] We also recently reported that Tp′TiCl$_2$(OAr) [Tp = HB(pyrazolyl)$_3$; Ar = Ph, 2-^{i}PrC$_6$H$_4$, 2,6-Me$_2$C$_6$H$_3$, 2,6-^{i}Pr$_2$C$_6$H$_3$, 2,6-Ph$_2$C$_6$H$_3$, C$_6$F$_5$] exhibited moderate to remarkable catalytic activities for ethylene polymerization in the presence of MAO.[13,14] Moreover, the cationic complex, [Tp*TiMe(O-2,6-Me$_2$C$_6$H$_3$)]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$·2THF, polymerized ethylene affording polymer with unimodal distributions.[13a]

Since the resultant polymers prepared by Tp′TiCl$_2$(OAr)−MAO catalysts were broad and affected by the Al/Ti molar ratios, we thus focus on using the dimethyl complexes in place of the dichloride analogues to explore the catalytically active species in this catalysis. We already succeeded in preparing Tp*TiMe$_2$(OAr) [Ar = 2,6-Me$_2$C$_6$H$_3$ (**2a**), 2,6-^{i}Pr$_2$C$_6$H$_3$ (**2b**)], [Tp*TiMe(O-2,6-Me$_2$C$_6$H$_3$)]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$·2THF (**3a**),[13a] therefore, we herein present our results in ethylene polymerization using the dimethyl analogues in the presence of various cocatalysts (Scheme 1). In particular, we wish to demonstrate that (1) ethylene polymerization using **2a**,**b**−MAO catalyst systems proceed in a quasi living manner, and (2) the cationic complex (**3a**) polymerizes ethylene even in the presence of Al(n-octyl)$_3$ affording high molecular weight polymers with unimodal distributions.

Results and Discussion

Ethylene polymerizations using Tp*TiX$_2$(OAr) [X = Cl (**1**), Me (**2**); Ar = 2,6-Me$_2$C$_6$H$_3$ (**a**), 2,6-^{i}Pr$_2$C$_6$H$_3$ (**b**)] were conducted in toluene in the presence of MAO, and the results are summarized in Table 1.[15] MAO was prepared as a white solid by removing toluene and AlMe$_3$ from commercially available MAO (PMAO, Tosoh Finechem Co.) and was chosen as the cocatalyst, because it was effective in the preparation of high molecular weight ethylene/α-olefin copolymers with unimodal molecular weight distributions when the Cp* analogue was used as the catalyst precursor.[7]

Although the resultant polymers prepared by Tp*TiCl$_2$(OAr) (**1a**,**b**)-MAO catalyst systems possessed broad molecular weight distributions (M_w/M_n = 40, 189),[15] the resultant polymers prepared by the dimethyl analogues possessed unimodal molecular weight distributions in all cases, irrespective of the polymerization temperature, Al/Ti molar ratios (M_w/M_n = 1.1−2.0; runs 2−12, 14−25).[15] The catalytic activities were affected by the Al/Ti molar ratios, and the polymerization temperature. No remarkable differences in the catalytic activities were observed between the dimethyl analogue (**2a**) and diisopropyl analogue (**2b**) under the optimized conditions [activity at 25 °C: 285−303 kg-PE/mol-Ti·h (runs 4−6, by **2a**) vs 279 kg-PE/mol-Ti·h (run 18, by **2b**)].

Note that the molecular weight distributions in the resultant polymers prepared by **2a** (at 0, 25 °C) or **2b** (at −30 to +25 °C) were narrow (M_w/M_n = 1.1−1.5, runs 2−10, runs 14−24).[16] The facts are unique contrasts to those observed using **1a**,**b**−MAO catalyst systems. These results clearly indicate that uniform catalytically active species play a role in the ethylene polymerization using **2a**,**b**−MAO catalysts, whereas several catalytically active species were formed in the polymerizations by **1a**,**b**−MAO catalysts. The activity decreased when the polymerizations were

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conducted at 50 °C, and the molecular weight distribution became broad but unimodal distributions ($M_w/M_n = 1.9-2.0$, runs 11,12,25). The activity also decreased when these polymerizations were conducted at low temperature (0, −10, and −30 °C).[15,16]

Note that the first order linear relationships between the M_n values and the polymer yields were obtained (Figure 1, Al/Ti = 250, molar ratio),[15] consistently with relatively low PDI values ($M_w/M_n = 1.1-1.4$, after 5 min).[15] The facts clearly indicate that these polymerizations proceeded in a quasi living manner under these conditions.[17,18]

Scheme 1

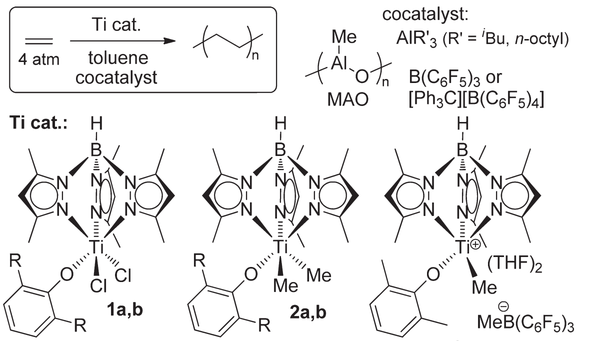

Table 2 summarizes results for ethylene polymerization by **2a**, **b**−$B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ catalyst systems in the presence of Al^iBu_3 or $Al(n\text{-octyl})_3$.[15] The catalytic activities were affected by the Al/Ti molar ratios employed, and $Al(n\text{-octyl})_3$, which should be the weak reagent for alkylation and/or chain transfer to Al, was also effective in this catalysis. The activity was optimized under certain molar ratios of both Al alkyls and $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$; the polymerizations did not take place in the absence of Al alkyls (runs 26, 32). The resultant polymers possessed relatively narrow, unimodal molecular weight distributions, suggesting that these polymerizations proceeded with uniform catalytically active species. The catalytic activities by **2b**−$[Ph_3C][B(C_6F_5)_4]$ catalyst systems [in the presence of Al^iBu_3 or $Al(n\text{-octyl})_3$] did not decrease after 15 min, but the M_n values in the resultant polymers were similar and were affected by the time course (runs 43−45, 47,48). The facts suggest that certain degree of chain transfer accompanied in these catalyzes. No remarkable differences in the activities were observed between **2a** and **2b** under the optimized conditions [activity at 25 °C: 255, 252 kg-PE/mol-Ti·h (runs 27,36, by **2a**) vs 219, 213 kg-PE/mol-Ti·h (runs 49,50, by **2b**)].

Ethylene Polymerization by $[Tp^*TiMe(O\text{-}2,6\text{-}Me_2C_6H_3)]^+[MeB(C_6F_5)_3]^-\cdot 2THF$ (3a). We previously reported that

Table 1. Ethylene Polymerization by $Tp^*TiX_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [X = Cl (1), Me (2); R = Me (a), ^{i}Pr (b)]-MAO Catalyst Systems[a],[15]

run	complex	MAO/mmol (Al/Ti)[b]	temp/ °C	time/min	yield/mg	activity[c]	$M_w{}^d \times 10^{-5}$	$M_n{}^d \times 10^{-5}$	$M_w/M_n{}^d$
1[e]	**1a**	0.50 (250)	25	10	138	414	3.83		40
2	**2a**	0.10 (50)	25	10	74	222	2.19	1.56	1.4
3	**2a**	0.15 (75)	25	10	79	237	2.12	1.63	1.3
4	**2a**	0.20 (100)	25	10	95	285	2.04	1.57	1.3
5	**2a**	0.25 (125)	25	10	101	303	1.86	1.43	1.3
6	**2a**	0.50 (250)	25	10	98	294	2.10	1.62	1.3
7	**2a**	0.75 (375)	25	10	70	210	1.68	1.40	1.2
8	**2a**	1.0 (500)	25	10	62	186	1.84	1.42	1.3
9	**2a**	0.50 (250)	0	10	36	108	2.91	2.24	1.3
10	**2a**	0.50 (250)	0	15	58	116	3.66	3.33	1.1
11	**2a**	0.50 (250)	50	5	31	186	2.15	1.08	2.0
12	**2a**	0.50 (250)	50	10	52	156	2.68	1.41	1.9
13[e]	**1b**	0.50 (250)	25	10	34	100	7.98		189
14	**2b**	0.10 (50)	25	10	60	180	1.79	1.19	1.5
15	**2b**	0.20 (100)	25	10	70	210	1.69	1.30	1.3
16	**2b**	0.30 (150)	25	10	63	189	1.44	1.03	1.4
17	**2b**	0.40 (200)	25	10	68	204	1.79	1.38	1.3
18	**2b**	0.50 (250)	25	10	93	279	1.66	1.38	1.2
19	**2b**	1.0 (500)	25	10	87	261	1.60	1.23	1.3
20	**2b**	2.0 (1000)	25	10	66	198	1.79	1.38	1.3
21	**2b**	0.50 (250)	0	10	61	183	2.79	2.15	1.3
22	**2b**	0.50 (250)	0	15	92	184	3.65	3.04	1.2
23	**2b**	0.50 (250)	−10	10	53	159	0.84	0.56	1.5
24	**2b**	0.50 (250)	−30	10	43	129	0.35	0.23	1.5
25	**2b**	0.50 (250)	50	10	43	129	3.17	1.59	2.0

[a] Conditions: complex 2.0 μmol, toluene 30 mL, MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO), ethylene 4 atm. [b] Molar ratio of Al/Ti. [c] Activity = kg polymer/mol-Ti·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards. [e] Cited from ref 13a.

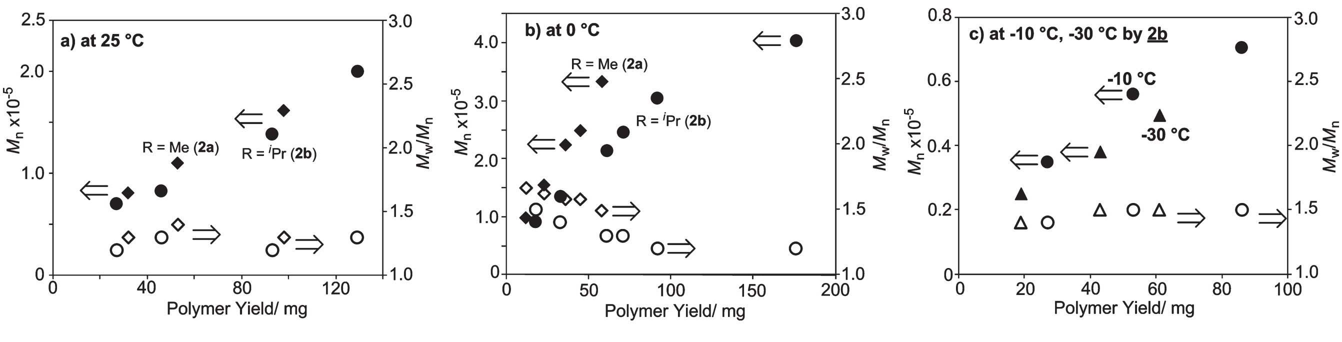

Figure 1. Plots of M_n vs polymer yields in ethylene polymerization by $Tp^*TiMe_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**2a**: ◆, ◇) or $Tp^*TiMe_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$− (**2b**: ●, ○; ▲, △)-MAO catalyst systems.[15].

Table 2. Ethylene Polymerization by $Tp^*TiMe_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [R = Me (**2a**), ^{i}Pr (**2b**)]-$B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ Catalyst Systems[a]

run	complex	B cocatal (B/Ti)[b]	Al/ μmol (Al/Ti)[b]	time/min	yield/mg	activity[c]	M_w[d] × 10^{-5}	M_n[d] × 10^{-5}	M_w/M_n[d]
26	**2a**	$B(C_6F_5)_3$ (1.0)	none	10	0				
27	**2a**	$B(C_6F_5)_3$ (1.0)	Al^iBu_3 50 (25)	10	85	255	2.74	1.83	1.5
28	**2a**	$B(C_6F_5)_3$ (1.0)	Al^iBu_3 100 (50)	10	57	171	3.69	1.68	2.2
29	**2a**	$B(C_6F_5)_3$ (1.0)	Al(*n*-octyl)$_3$ 50 (25)	10	55	165	2.76	1.73	1.6
30	**2a**	$B(C_6F_5)_3$ (3.0)	Al(*n*-octyl)$_3$ 50 (25)	10	79	237	2.84	2.18	1.3
31	**2a**	$B(C_6F_5)_3$ (1.0)	Al(*n*-octyl)$_3$ 100 (50)	10	39	117	2.51	1.57	1.6
32	**2a**	$[Ph_3C][B(C_6F_5)_4]$ (1.0)	none	10	0				
33	**2a**	$[Ph_3C][B(C_6F_5)_4]$ (1.0)	Al^iBu_3 100 (50)	10	21	63	11.2	3.50	3.2
34	**2a**	$[Ph_3C][B(C_6F_5)_4]$ (1.0)	Al^iBu_3 200 (100)	10	20	60	12.9	3.15	4.1
35	**2a**	$[Ph_3C][B(C_6F_5)_4]$ (1.0)	Al(*n*-octyl)$_3$ 50 (25)	10	53	159	2.31	1.36	1.7
36	**2a**	$[Ph_3C][B(C_6F_5)_4]$ (3.0)	Al(*n*-octyl)$_3$ 50 (25)	10	84	252	2.14	1.53	1.4
37	**2a**	$[Ph_3C][B(C_6F_5)_4]$ (1.0)	Al(*n*-octyl)$_3$ 100 (50)	10	36	103	2.21	1.23	1.8
38	**2b**	$B(C_6F_5)_3$ (1.0)	Al^iBu_3 50 (25)	10	30	90	1.73	1.33	1.3
39	**2b**	$B(C_6F_5)_3$ (1.0)	Al^iBu_3 100 (50)	10	28	84	1.77	1.36	1.3
40	**2b**	$B(C_6F_5)_3$ (1.0)	Al(*n*-octyl)$_3$ 50 (25)	10	26	78	1.74	1.16	1.5
41	**2b**	$B(C_6F_5)_3$ (3.0)	Al(*n*-octyl)$_3$ 50 (25)	10	44	132	1.01	0.72	1.4
42	**2b**	$B(C_6F_5)_3$ (1.0)	Al(*n*-octyl)$_3$ 100 (50)	10	27	81	1.81	1.21	1.5
43	**2b**	$[Ph_3C][B(C_6F_5)_4]$ (1.0)	Al^iBu_3 50 (25)	5	13	78	1.43	1.10	1.3
44	**2b**	$[Ph_3C][B(C_6F_5)_4]$ (1.0)	Al^iBu_3 50 (25)	10	29	87	1.55	1.03	1.5
45	**2b**	$[Ph_3C][B(C_6F_5)_4]$ (1.0)	Al^iBu_3 50 (25)	15	36	72	1.81	1.29	1.4
46	**2b**	$[Ph_3C][B(C_6F_5)_4]$ (3.0)	Al^iBu_3 50 (25)	10	38	114	0.71	0.55	1.3
47	**2b**	$[Ph_3C][B(C_6F_5)_4]$ (1.0)	Al(*n*-octyl)$_3$ 50 (25)	5	18	108	1.02	0.60	1.7
48	**2b**	$[Ph_3C][B(C_6F_5)_4]$ (1.0)	Al(*n*-octyl)$_3$ 50 (25)	15	46	92	1.54	0.96	1.6
49	**2b**	$[Ph_3C][B(C_6F_5)_4]$ (3.0)	Al(*n*-octyl)$_3$ 50 (25)	10	73	219	1.60	1.14	1.4
50	**2b**	$[Ph_3C][B(C_6F_5)_4]$ (3.0)	Al(*n*-octyl)$_3$ 100 (50)	10	71	213	1.53	1.02	1.5

[a] Conditions: complex 2.0 μmol, toluene 30 mL, ethylene 4 atm, 25 °C. [b] B/Ti or Al/Ti molar ratio. [c] Activity = kg-PE/mol-Ti·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards.

Table 3. Ethylene Polymerization by $[Tp^*TiMe(O\text{-}2,6\text{-}Me_2C_6H_3)]^+[MeB(C_6F_5)_3]^-\cdot 2THF$ (**3a**)[a]

run	Al/μmol (Al/Ti)[b]	time/min	temp/ °C	yield/mg	activity[c]	M_w[d] × 10^{-5}	M_n[d] × 10^{-5}	M_w/M_n[d]
51	none	10	25	trace				
52	Al(*n*-octyl)$_3$ 10 (5)	10	25	trace				
53	Al(*n*-octyl)$_3$ 50 (25)	10	25	61	183	1.92	1.20	1.6
54	Al(*n*-octyl)$_3$ 100 (50)	10	25	57	171	1.90	1.36	1.4
55	Al(*n*-octyl)$_3$ 200 (100)	10	25	48	144	1.64	1.09	1.5
56	Al(*n*-octyl)$_3$ 50 (25)	5	25	42	252	2.25	1.61	1.4
57	Al(*n*-octyl)$_3$ 50 (25)	15	25	65	130	2.14	1.43	1.5
58	Al(*n*-octyl)$_3$ 50 (25)	10	40	70	210	2.43	1.43	1.7
59	Al(*n*-octyl)$_3$ 50 (25)	10	55	33	99	1.10	0.35	3.1
60[e]	Al^iBu_3 50 (25)	10	25	90	270	3.95	1.98	2.0
61[e]	Al^iBu_3 200 (100)	10	25	43	129	4.25	1.12	3.8
62	Al^iBu_3 50 (25)	10	40	25	75	1.42	0.57	2.5
63	Al^iBu_3 50 (25)	10	55	9	27	0.76	0.22	3.5

[a] Conditions: complex 2.0 μmol, toluene 30 mL, ethylene 4 atm. [b] Molar ratio of Al/Ti. [c] Activity = kg-PE/mol-Ti·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards. [e] Cited from ref 13a.

$[Tp^*TiMe(O\text{-}2,6\text{-}Me_2C_6H_3)]^+[MeB(C_6F_5)_3]^-\cdot 2THF$ (**3a**), which could be isolated as a THF adduct by treating **2a** with $[Ph_3C][B(C_6F_5)_4]$ in THF,[13a,19−21] showed moderate catalytic activity (very close to that by **2a** in the presence of MAO, conducted under the same conditions as run 6, Table 1) without MAO (in the presence of small amount of Al^iBu_3), affording polyethylene with a uniform molecular weight distribution (run 60, Table 3).[13a] The result thus clearly suggested that the cationic complex (**3a**) plays an important role as the catalytically active species in this catalysis. Since the polymerization did not take place in the absence of Al^iBu_3, also since the activity decreased affording polymer with a broad molecular weight distribution upon increasing Al/Ti molar ratio (Al/Ti = 100, M_w/M_n = 3.8, run 61)[13a] probably due to decomposition of the active species by Al^iBu_3, the ethylene polymerizations by **3a** in the presence of Al(*n*-octyl)$_3$, which should be the weak reagent for alkylation and/or chain transfer, were conducted at various Al/Ti molar ratios to explore the role of Al alkyl in details. The results are summarized in Table 3.[15,17−19]

It was revealed that the cationic complex (**3a**) polymerizes ethylene in the presence of Al(*n*-octyl)$_3$, and the activity was affected by the Al/Ti molar ratio. The resultant polymers prepared at 25 °C possessed unimodal molecular weight distributions (M_w/M_n = 1.4−1.6), suggesting that these polymerizations proceeded by uniform catalytically active species. The catalytic activity by **3a** at 40 °C was higher than that performed at 25 °C, but the activity decreased at 55 °C probably due to partial decomposition of the catalytically active species, assumed by broad molecular weight distribution in the resultant polyethylene (M_w/M_n = 3.1). The activity under the optimized conditions (Al/Ti = 25) after 10 min (activity 183 kg-PE/mol-Ti·h, run 53) was somewhat lower than that by **2a** in the presence of both Al(*n*-octyl)$_3$ and $B(C_6F_5)_3$ [activity 237 kg-PE/mol-Ti·h, run 30, molar ratio of Ti/Al/*B* = 1/25/3]. This is because that the observed activity by **3a** decreased gradually over time course (5−15 min, runs 53,56,57). The initial activity after 5 min was 252 kg-PE/mol-Ti·h, and the value is similar to that in the presence of Al^iBu_3 and those by **2a** in the presence of both Al(*n*-octyl)$_3$ and $B(C_6F_5)_3$. As described above, significant decrease in the activity over time course was not observed in the polymerization by **2a** in the presence of cocatalysts (Tables 1 and 2), and the exact reason is uncertain at this moment.

Table 4 summarizes the results in ethylene polymerization using **2a** and **3a** under the optimized conditions. It is clear that both the observed catalytic activities and the molecular

Table 4. Summary of Selected Ethylene Polymerization Results by $Tp^*TiMe_2(O\text{-}2,6\text{-}MeR_2C_6H_3)$ (2a), $[Tp^*TiMe(O\text{-}2,6\text{-}Me_2C_6H_3)]^+[MeB(C_6F_5)_3]^- \cdot 2THF$ (3a)[a]

run	complex	cocatalyst(s) (molar ratio)[b]	activity[c]	$M_w{}^d \times 10^{-5}$	$M_n{}^d \times 10^{-5}$	$M_w/M_n{}^d$
6	**2a**	MAO (25)	294	2.10	1.62	1.3
27	**2a**	$B(C_6F_5)_3$ (1.0)/ Al^iBu_3 (25)	255	2.74	1.83	1.5
30	**2a**	$B(C_6F_5)_3$ (3.0)/ Al(*n*-octyl)$_3$ (25)	237	2.84	2.18	1.3
36	**2a**	$[Ph_3C][B(C_6F_5)_4]$ (3.0)/ Al(*n*-octyl)$_3$ (25)	252	2.14	1.53	1.4
60	**3a**	Al^iBu_3 (25)	270	3.95	1.98	2.0
56	**3a**	Al(*n*-octyl)$_3$ (25)	252	2.25	1.61	1.4

[a] Conditions: complex 2.0 μmol, toluene 30 mL, ethylene 4 atm, 5 or 10 min . [b] Molar ratio based on Ti. [c] Activity = kg-PE/mol-Ti·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards.

weights in the resultant polymers are close, although the polymerization by **2a** - MAO catalyst took place in a living manner. Moreover, reaction of **2a** with $[Ph_3C][B(C_6F_5)_4]$ in THF afforded **3a** exclusively.[13a] The facts thus suggest that the similar catalytically active species may play a role in this catalysis. In particular, **3a** polymerizes ethylene even in the presence of Al(*n*-octyl)$_3$, it is thus concluded that the cationic alkyl species play a role as the active species in this catalysis. It also turned out throughout this study that effect of cocatalyst play roles for stabilizing the catalytically active species and the polymerization behavior. We believe that these information should be important for designing molecular catalysts for precise olefin polymerization in the absence of (excess amount of) cocatalysts.

Experimental Section

General Experimental Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. All chemicals used were of reagent grades and were purified by standard purification procedures. Anhydrous grade toluene and *n*-hexane (Kanto Chemical Co., Inc.) were stored in the drybox in the presence of molecular sieves (mixture of 3A 1/16 and 4A 1/8, and 13X 1/16) after passing through an alumina short column under nitrogen. $B(C_6F_5)_3$ (Aldrich), $[Ph_3C][B(C_6F_5)_4]$ (Asahi Glass Co., Ltd.) and Al^iBu_3 (Kanto Chemical Co., Inc.) were stored in the drybox and were used as received. Ethylene of polymerization grade (Sumitomo Seika Chemicals, Ltd.) was used as received without further purification. Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C for removing toluene, $AlMe_3$, and then heated at > 100 °C for 1 h for completion) in the drybox to give white solids. $Tp^*TiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**1a**), $Tp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1b**), $Tp^*TiMe_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**2a**), $Tp^*TiMe_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**2b**), and $Tp^*TiMe(O\text{-}2,6\text{-}Me_2C_6H_3)][MeB(C_6F_5)_3] \cdot 2THF$ (**3a**) were prepared according to our previous report.[13a]

All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.78 MHz for ^1H and 100.53 MHz for ^{13}C). All spectra were obtained in the solvent indicated at room temperature unless otherwise noted. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00, ^1H, ^{13}C).

Molecular weights and molecular weight distributions for the poly(ethylene) were measured by gel permeation chromatography (GPC, Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature, Tosoh Co.) with polystyrene gel column (TSK gel GMH_{HR}-H HTX2, 30 cm × 7 .8 mm i.d.), ranging from $< 10^2$ to $< 2.8 \times 10^8$ MW) at 140 °C using *o*-dichlorobenzene containing 0.05% w/v 2,6-di-*tert*-butyl-*p*-cresol as the solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

Ethylene Polymerization Using MAO as a Cocatalyst. A typical reaction procedure for ethylene homopolymerization using MAO cocatalyst (run 4, Table 1), is as follows. Toluene (29 mL), and MAO solid (11.6 mg, 0.20 mmol) were added into the autoclave (100 mL scale, stainless steel) in the drybox, and the reaction apparatus was then replaced, filled with ethylene (1 atm) at 25 °C. A toluene solution (1.0 mL) containing **2a** (2.0 μmol) was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 3 atm (total ethylene pressure 4 atm). The mixture was magnetically stirred for 10 min, ethylene remained was purged after the reaction, and the mixture was then poured into MeOH (300 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with MeOH, and was then dried *in vacuo* at 60 °C.

Polymerization procedure by **2a**,**b**−$[Ph_3C][B(C_6F_5)_4]$ or $B(C_6F_5)_3-Al^iBu_3$ or Al(*n*-octyl)$_3$ catalyst systems were similar to those by **2a**,**b**−MAO catalyst systems except that a toluene solution containing $[Ph_3C][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ was added after introduction of a toluene solution containing **2a**,**b**. Ethylene polymerization procedure by **3a** was the same as that by **2a**−MAO catalyst system except that prescribed amount of Al(*n*-octyl)$_3$ was used in place of MAO.

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Supporting Information Available: Additional ethylene polymerization data using $Tp^*TiMe_2(OAr)$ [Ar = 2,6-$Me_2C_6H_3$ (**2a**), 2,6-$^iPr_2C_6H_3$ (**2b**)]-cocatalyst systems and $[Tp^*TiMe(O\text{-}2,6\text{-}Me_2C_6H_3)]^+-[MeB(C_6F_5)_3]^- \cdot 2THF$ (**3a**) in the presence of Al alkyls. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Additional ethylene polymerization data using Tp*$TiMe_2(OAr)$ [Ar = $2,6\text{-}Me_2C_6H_3$ (**2a**), $2,6\text{-}{}^iPr_2C_6H_3$ (**2b**)] − cocatalyst systems, and [Tp*$TiMe(O\text{-}2,6\text{-}Me_2C_6H_3)]^+\text{-}[MeB(C_6F_5)_3]^-$·2THF (**3a**) in the presence of Al alkyls are shown in the Supporting Information.

(16) The molecular weights in the resultant polymer prepared at 0 °C were somewhat higher than those prepared at +25, −10, and −30 °C. The polymerization results by **2a,b** at 0 °C were reproducible, we are not sure why the M_n values for the resultant polymers were higher than the others at the certain period. Moreover, the catalyst efficiencies (estimated from both the polymer yields and the M_n values) were low in all cases.

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