

Effect of Borate Cocatalysts toward Activity and Comonomer Incorporation in Ethylene Copolymerization by Half-Titanocene Catalysts in Methylcyclohexane

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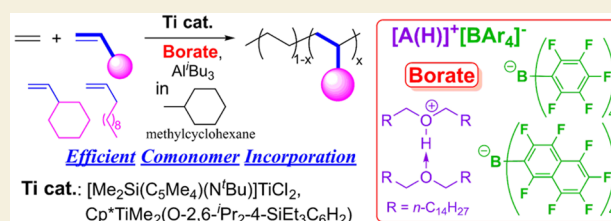
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ABSTRACT: Ethylene copolymerizations with 2-methyl-1-pentene, 1-dodecene (DD), vinylcyclohexane (VCH), $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^+\text{tBu})\text{TiCl}_2$ (**1**), $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-iPr}_2-4\text{-RC}_6\text{H}_2)$ [$\text{R} = \text{H}$ (**2**), SiEt_3 (**3**)]–borate, and $[\text{A}(\text{H})]^+[\text{BAr}_4]^-$ [$\text{Ar} = \text{C}_6\text{F}_5$; $\text{A}(\text{H})^+ = \text{N}^+(\text{H})\text{Me}(n\text{-C}_{18}\text{H}_{37})_2$, $\text{N}^+(\text{H})(\text{CH}_2\text{CF}_3)(n\text{-C}_{18}\text{H}_{37})_2$, $\text{HO}^+(n\text{-C}_{14}\text{H}_{29})_2\cdot\text{O}(n\text{-C}_{14}\text{H}_{29})_2$, $\text{HO}^+(n\text{-C}_{16}\text{H}_{33})_2\cdot\text{O}(n\text{-C}_{16}\text{H}_{33})_2$; $\text{Ar} = \text{C}_{10}\text{F}_7$, $\text{A}(\text{H})^+ = \text{HO}^+(n\text{-C}_{14}\text{H}_{29})_2\cdot\text{O}(n\text{-C}_{14}\text{H}_{29})_2$ (**BS**), $\text{N}^+(\text{H})(\text{CH}_2\text{CF}_3)(n\text{-C}_{18}\text{H}_{37})_2$] catalyst systems conducted in methylcyclohexane (MCH) exhibited better comonomer incorporation than those conducted in toluene (in the presence of methylaluminumoxane (MAO) or borate cocatalysts). The activity was affected by the borate cocatalyst and 1,3–**B5** catalyst systems in MCH and showed the highest activity in the ethylene copolymerizations with VCH and DD.

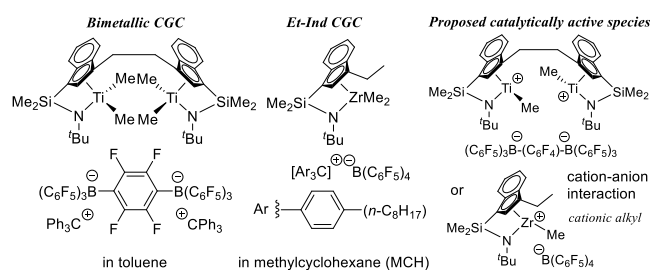
KEYWORDS: polymerization, borate cocatalyst, titanium, ethylene copolymerization, cation–anion interaction, half-titanocene



Olefin polymerization is the core technology for production of polyolefins (such as linear high/low density polyethylene, isotactic polypropylene), widely used synthetic polymers in our daily life. It has been recognized that the catalyst development provides a new possibility for synthesis of new polymers and/or the more efficient process.^{1–10} It has been proposed that the cationic metal alkyl species, generated from group 4 transition metal complexes such as metallocenes ($\text{Cp}'_2\text{MX}_2$; $\text{Cp}' = \text{cyclopentadienyl}$; $\text{M} = \text{Ti, Zr, Hf}$; $\text{X} = \text{Cl, Me, etc.}$),^{1–3} linked half-titanocenes exemplified as $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^+\text{tBu})\text{TiCl}_2$ (**1**),⁴ or modified half-titanocenes [$\text{Cp}'\text{TiX}_2(\text{Y})$, $\text{Y} = \text{anionic ancillary donor}$]^{5–8} by treatment with methylaluminumoxane (MAO) or borate cocatalysts, play an essential role in this catalysis.^{1–13}

The cation/anion interaction,^{14–22} called the catalyst–cocatalyst nuclearity effect,^{19–21} has been known to affect the activity and the comonomer incorporation in the ethylene copolymerization. Remarkable improvements in the comonomer incorporation were first demonstrated by the bimetallic catalyst system,^{16–18,21} ethylene bridged linked half-titanocene, $(\text{CH}_2\text{CH}_2)[\text{Me}_2\text{Si}(\text{indenyl})(\text{N}^+\text{tBu})]_2\text{Ti}_2\text{Me}_4$ (bimetallic CGC, **Chart 1**), activated with $[\text{Ph}_3\text{C}]_2[1,4\text{-(C}_6\text{F}_5)_3\text{BC}_6\text{F}_4\text{B}(\text{C}_6\text{F}_5)_3]$ in the copolymerization with 1-octene,¹⁶ isobutene,¹⁶ methylcyclopentane,¹⁷ and with styrene in toluene.¹⁸ It was reported later that the ethylene/1-hexene copolymerization by the ethyl-indenyl zirconium analogue (Et-Ind CGC, **Chart 1**) activated with $[\{4\text{-(}n\text{-C}_8\text{H}_{17}\text{)C}_6\text{H}_4\}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ conducted in methylcyclohexane (MCH) showed higher catalytic activity

Chart 1. Catalyst–Cocatalyst Nuclearity Effect in Ethylene Copolymerization by a Bimetallic (Bimetallic CGC) System in Toluene^{16–18} or Monomeric (Et-Ind CGC) System in Methylcyclohexane (MCH)²² and the Proposed Catalytically Active Cationic Alkyl Species (Right)



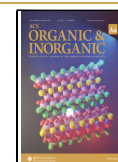
and better 1-hexene incorporation than that conducted in toluene.²² The better catalyst performance observed in the latter catalyst system was explained as due to the successful utilization of a weak interaction between the cation and the borate anion without coordination of toluene to the formed cationic alkyl species (**Chart 1**, right).^{22–25} The effect has been

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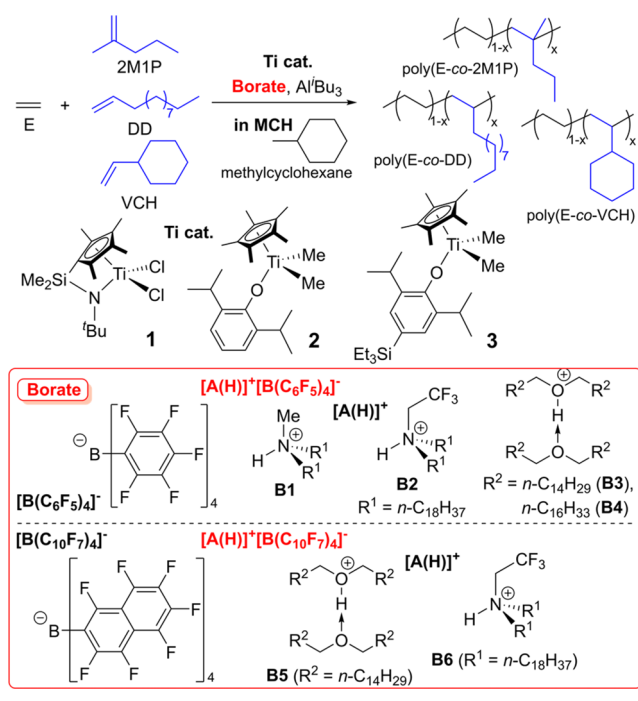
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considered as an important factor for design of the efficient catalyst system as well as better understanding of the reaction mechanism.^{26–32} However, the effect of borates including counteranions [$B(C_6F_5)_4^-$ vs $B(C_{10}F_7)_4^-$; $A(H)^+$ (ammonium salts, oxonium salts), Scheme 1] in the ethylene copolymerization, especially in alkane solvents, has not yet been well studied.

Scheme 1. Ethylene Copolymerization with 2-Methyl-1-pentene (2M1P), 1-Dodecene (DD), and Vinylcyclohexane (VCH) in Methylcyclohexane (MCH) by $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (1) and $Cp^*TiMe_2(O-2,6-^iPr_2-4-R'C_6H_2)$ [$R' = H$ (2), $SiEt_3$ (3)] in the Presence of Borate (B1–B6) Cocatalyst



We thus conducted an ethylene copolymerization study using half-titanocene catalysts in the presence of six *alkane soluble* borate compounds (B1–B6, Scheme 1), $[A(H)]^+[B(C_6F_5)_4]^-$ [$A(H)^+ = N^+(H)Me(n-C_{18}H_{37})_2$ (B1),³³ $N^+(H)-$

$(CH_2CF_3)(n-C_{18}H_{37})_2$ (B2), $HO^+(n-C_{14}H_{29})_2 \cdot O(n-C_{14}H_{29})_2$ (B3), $HO^+(n-C_{16}H_{33})_2 \cdot O(n-C_{16}H_{33})_2$ (B4)] or $[A(H)]^+[B(C_{10}F_7)_4]^-$ [$A(H)^+ = HO^+(n-C_{14}H_{29})_2 \cdot O(n-C_{14}H_{29})_2$ (B5), $N^+(H)(CH_2CF_3)(n-C_{18}H_{37})_2$ (B6)], in MCH. Through this study, we wish to communicate an important role/effect of borate anion toward both the activity and the comonomer incorporation including the fact that *drastic* improvements in comonomer incorporation were observed by using these borate cocatalysts in MCH compared to those conducted in toluene.

Linked half-titanocene called constrained geometry type, $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (1), have been chosen in this study because 1 shows efficient comonomer incorporation especially of long chain α -olefins in the ethylene copolymerization.^{4,34–36} The phenoxide modified half-titanocenes, $Cp^*TiMe_2(O-2,6-^iPr_2-4-R'C_6H_2)$ [$R' = H$ (2), $SiEt_3$ (3)], have also been chosen because these catalysts display efficient comonomer incorporations in the ethylene (E) copolymerizations not only with 1-dodecene (DD)^{35–37} but also with 2-methyl-1-pentene (2M1P)^{38,39} and vinylcyclohexane (VCH),⁴⁰ which are not incorporated by the ordinary (metallocene) catalysts. The dimethyl complex (3) was newly prepared by treating Cp^*TiMe_3 with 2,6- $^iPr_2-4-SiEt_3C_6H_2OH$ in Et_2O according to the published method for synthesis of 2⁴¹ and was identified by NMR spectra and elemental analysis (shown in the Supporting Information, SI). Borate compounds (B1–B6, Scheme 1) have been chosen to explore the effect of the borate anion, $B(C_6F_5)_4^-$ or $B(C_{10}F_7)_4^-$, as well as of the counter cations, ammonium salts or oxonium salts, that would interact (as amine or ether) with the assumed cationic alkyl titanium species *in situ*.^{42,43}

Table 1 summarizes selected results in the E/2M1P copolymerization (ethylene 4 atm in MCH at 25 °C), and additional results are shown in Table S1 in the SI.⁴⁴ These copolymerizations in the presence of MAO or borate cocatalysts were conducted under the optimized conditions (amount of Al cocatalyst).^{36,39,45} MCH has also been chosen due to better solubility of borate compounds (B1–B6).

It was revealed that the activity by 1 was affected by the borate cocatalyst employed and increased in the following order: activity = 149 kg-polymer/mol-Ti·h (B1, run S1) < 768 (B6, run S7) < 2660 (B5, run S6) < 3770 (B2, run S2) < 6810 (B3, run 1). The activity in the presence of B3 was rather higher than that conducted in toluene in the presence of MAO

Table 1. Copolymerization of Ethylene (E) with 2-Methyl-1-pentene (2M1P) by $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (1) or $Cp^*TiMe_2(O-2,6-^iPr_2-4-R'-C_6H_2)$ [$R = H$ (2), $SiEt_3$ (3)]–Borate Cocatalyst Systems^a

run	cat. (μ mol)	solvent	Al cocat.	borate	yield/mg	activity ^b	$M_n^c \times 10^{-4}$	M_w/M_n^c	$T_m^d / ^\circ C$	2M1P ^e /mol %
1	1 (1.0)	MCH	Al^iBu_3 ^f	B3	1135	6810	44.9	6.42	120	0.4
2	1 (0.1)	toluene	MAO	---	84.8	5090	32.4	3.66	129	
3	2 (1.0)	MCH	Al^iBu_3	B3	702	4210	6.28	1.93	99.0	5.5
4	2 (1.0)	MCH	Al^iBu_3	B5	710	4260	5.76	1.76	93.6	6.8
5	2 (0.05)	toluene	MAO	---	93.3	11200	8.41	2.25	111	2.6
6	3 (1.0)	MCH	Al^iBu_3	B2	446	2680	3.82	1.96	98.7	
7	3 (1.0)	MCH	Al^iBu_3	B3	673	4040	4.11	1.90	101	5.0
8	3 (1.0)	MCH	Al^iBu_3	B4	664	3980	3.21	2.41	98.4	
9	3 (1.0)	MCH	Al^iBu_3	B5	843	5060	5.41	1.84	97.9	6.0
10	3 (0.05)	toluene	MAO	---	155	18600	8.34	2.05	109	3.1

^aConditions: MCH (methylcyclohexane) or toluene and 2-methyl-1-pentene (2M1P) 1.35 M (5.0 mL) total 30.0 mL, Al^iBu_3 [0.55 mmol/L hexane, Al/Ti = 1000 (molar ratio)] or MAO 3.0 mmol (Al/Ti = 60000, molar ratio), borate (borate/Ti molar ratio = 1.0), ethylene 4 atm, 25 °C, 10 min. ^bActivity = kg-polymer/mol-Ti·h. ^cGPC data in *o*-dichlorobenzene vs polystyrene standards (M_n in g/mol). ^dBy DSC thermograms. ^e2M1P content (mol %) estimated by ¹³C NMR spectra. ^fAl/Ti = 500, molar ratio.

Table 2. Copolymerization of Ethylene (E) with 1-Dodecene (DD) by $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ (1) or $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-iPr}_2\text{-4-SiEt}_3\text{-C}_6\text{H}_2)$ (3)–Cocatalyst Systems^a

run	cat. (μmol)	solvent	Al cocat.	borate	yield/mg	activity ^b	$M_n^c \times 10^{-4}$	M_w/M_n^c	$T_m^d/^\circ\text{C}$	DD ^e /mol %
11	1 (0.1)	MCH	Al^iBu_3	B2	343	34300	17.6	2.72	−35.6	14.1
12	1 (0.1)	MCH	Al^iBu_3	B3	241	24100	14.3	2.87	−35.3	14.1
13	1 (0.1)	MCH	Al^iBu_3	B5	485	48500	15.9	2.53	−36.4	14.0 (14.7) ^f
14	1 (0.05)	toluene	MAO	---	190	38000	73.5	4.51	31.8	7.2
15	3 (0.05)	MCH	Al^iBu_3	B2	123	24600	8.79	1.86	−40.7	13.7
16	3 (0.05)	MCH	Al^iBu_3	B3	232	46400	10.2	1.93	−40.6	13.7
17	3 (0.05)	MCH	Al^iBu_3	B5	311	62200	11.6	1.95	−38.7	13.8
18	3 (0.001)	toluene	MAO	---	242	2420000	20.0	2.60	37.3	6.8

^aConditions: MCH (methylcyclohexane) or toluene and 1-dodecene (DD) 0.45 M (3.0 mL) total 30.0 mL, Al^iBu_3 [0.55 mmol/L hexane, Al/Ti = 1000 (molar ratio)] or MAO 2.0 mmol (Al/Ti 2000, molar ratio), borate (borate/Ti molar ratio = 1.0), ethylene 6 atm, 25 °C, 6 min. ^bActivity = kg-polymer/mol-Ti-h. ^cGPC data in *o*-dichlorobenzene vs polystyrene standards (M_n in g/mol). ^dBy DSC thermograms. ^eDD content (mol %) estimated by ¹H NMR spectra. ^fDD content (mol %) estimated by ¹³C NMR spectra.

Table 3. Ethylene Copolymerization with Vinylcyclohexane (VCH) by $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ (1) or $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-iPr}_2\text{-4-SiEt}_3\text{-C}_6\text{H}_2)$ (3)–Cocatalyst Systems^a

run	cat. (μmol)	borate (B/Ti) ^b	VCH ^c /M	yield/mg	activity ^d	$M_n^e \times 10^{-4}$	M_w/M_n^e	$T_m, (T_g)^f/^\circ\text{C}$	VCH ^g /mol %
19	1 (0.05)	B2 (1.0)	0.73	154	30800	10.4	1.82	95.4	5.4
20	1 (0.05)	B2 (1.0)	1.22	84	16800	7.70	1.70	87.5	8.8
21	1 (0.05)	B3 (1.0)	0.73	254	50800	9.65	1.90	97.7	
22	1 (0.05)	B3 (1.0)	1.22	220	44000	6.31	1.65	86.0	9.0
23	1 (0.25)	B4 (1.0)	1.22	264	10600	5.93	1.75	87.0	8.7
24	1 (0.25)	B4 (3.0)	1.22	565	22600	5.87	1.91	86.2	9.0
25	1 (0.05)	B5 (1.0)	1.22	345	69000	8.65	1.98	81.4	9.7
26	1 (0.05)	B5 (2.0)	1.22	474	94800	9.32	2.00	83.1	9.4
27	1 (0.05)	B5 (3.0)	1.22	762	152000	8.50	1.98	85.3	9.1
28	1 (0.05)	B5 (1.0)	1.83	147	29400	6.43	1.85	73.8 (−17.0)	12.7
29	1 (0.05)	B5 (1.0)	2.44	89	17800	5.63	1.73	62.9 (−16.9)	15.9
30 ^h	1 (0.05)	---	1.22	197	39400	21.4	3.38	92.5	6.0
31	3 (0.05)	B2 (1.0)	1.22	170	34000	9.71	1.78	(−6.4)	
32	3 (0.05)	B2 (3.0)	1.22	654	131000	7.41	1.79	(−0.8)	
33	3 (0.05)	B3 (3.0)	1.22	727	145400	7.82	1.90	(−0.1)	32.2
34	3 (0.05)	B4 (3.0)	1.22	749	150000	6.41	1.94	(−7.8)	29.4
35	3 (0.05)	B5 (3.0)	1.22	818	164000	11.4	1.89	(1.6)	33.0
36 ^h	3 (0.01)	---	1.22	224	224000	17.5	2.43	(−15.1)	24.1

^aConditions: MCH (methylcyclohexane) and vinylcyclohexane (VCH) total 30.0 mL, Al^iBu_3 (0.55 mmol/L *n*-hexane, Al/Ti molar ratio = 1000), ethylene 6 atm, 25 °C, 6 min. ^bMolar ratio of borate (B) to Ti. ^cInitial VCH concentration in mmol/mL. ^dActivity = kg-polymer/mol-Ti-h. ^eGPC data in *o*-dichlorobenzene vs polystyrene standards (M_n in g/mol). ^fBy DSC thermograms. ^gVCH content (mol %) estimated by ¹³C NMR spectra. ^hMAO (Al/Ti = 2000, molar ratio) was used in place of Al^iBu_3 – borate cocatalyst, and the polymerization was conducted in toluene.

cocatalyst (5090 kg-polymer/mol-Ti-h; more data for comparison are shown in the S1), although we do not have a clear explanation for the effect of borate cocatalyst toward the activity. It was also revealed that the **1**–**B3** catalyst system showed 2M1P incorporation [0.4 mol %, as observed by the decrease in the melting temperature (T_m) in the DSC thermogram (Figure S54) and by the ¹³C NMR spectrum (Figure S23a)],⁴⁴ whereas the **1**–MAO catalyst system showed negligible 2M1P incorporation under the same conditions (estimated by the DSC thermogram, $T_m = 129$ °C).⁴⁴ It also seems that the 2M1P incorporations (estimated by the T_m values) were also affected by the borate cocatalyst employed (**B1** and **B6** showed rather low 2M1P incorporations compared to the others), whereas the resultant copolymers possessed sole T_m values (suggesting uniform composition, Figure S54).⁴⁴ The rather large PDI (M_w/M_n) values by **1** would be due to the heterogeneous nature of the reaction solution. It was also revealed that the activities of **2** and **3** were affected by the borate cocatalyst (**B1**–**B6**) employed. The **3**–**B5** catalyst system showed the highest activity (run 9, 5060 kg-

polymer/mol-Ti-h), and the resultant copolymer possessed higher 2M1P content than that conducted in toluene by the **1**–MAO catalyst system (6.0 mol % vs 3.1 mol %). In contrast, the activities in the presence of **B1** were low, affording polymers containing a composition with rather high T_m values (runs S19 and S35 in Table S1).⁴⁴ Moreover, **B5** showed better 2M1P incorporation than **B3** [2M1P 5.5 mol % (**B3**, run 3) vs 6.8 mol % (**B5**, run 4), 5.0 mol % (**B3**, run 7) vs 6.0 mol % (**B5**, run 9)]. It was shown that conducting these copolymerizations in MCH in the presence of borate cocatalysts (**B2**–**B6**) showed better 2M1P incorporation than conducting them in toluene in the presence of MAO. As reported previously (runs S30–S34 in Table S1),³⁹ 2M1P incorporations in the copolymerization using **2** or $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-iPr}_2\text{C}_6\text{H}_3)$ (**2-Cl**) in toluene were not affected by cocatalysts such as MAO, modified MAO, or Al^iBu_3 –borate systems (more data are shown in Table S1, runs S22–S30).⁴⁴ It was also revealed that, in the copolymerization by **2**, a critical optimization of Al/Ti molar ratios was required for obtaining of the copolymers with uniform compositions (without

contamination of polymer with negligible 2M1P incorporation) (runs 3, 4, and S12–S22 in Table S1);^{44,45} the SiEt₃ analogue (**3**), thus, is suited in terms of the copolymer synthesis with uniform compositions for the following study.

Table 2 summarizes selected results in the E/DD copolymerization (ethylene 6 atm, at 25 °C) by **1** and **3** in MCH in the presence of borate cocatalyst, and additional results are shown in Table S2.⁴⁴ It should be noted that the **1**–**B5** catalyst system in MCH showed higher activity with better DD incorporation than the **1**–MAO catalyst system in toluene (run 13 vs 14; activity 48500 vs 38000 kg-polymer/mol-Ti·h; DD content 14.0 mol % vs 7.2 mol %). Notable improvement in the DD incorporation was observed when these copolymerizations by **1** were conducted in MCH in the presence of borate cocatalysts (runs 11–13, S40, and S41 in Table S2), although the **1**–**B1** catalyst system showed inferior catalyst performance to the other systems.⁴⁴

Similarly, notable improvement in the DD incorporation was observed by **3** in MCH in the presence of borate cocatalyst (**B2**, **B3**, and **B5**, runs 15–17, and S43 in Table S2),⁴⁴ although the observed activities were apparently low compared to that for the incorporation conducted in toluene in the presence of MAO (run 18 in Table S2). The resultant copolymers prepared by the **1**–borate and **3**–borate catalyst systems possessed rather low M_n values probably due to the high DD content with unimodal molecular weight distributions ($M_n = 8.06\text{--}17.6 \times 10^4$, $M_w/M_n = 1.84\text{--}2.87$) as well as uniform compositions confirmed by DSC thermograms (Figures S59–S61).⁴⁴ As observed in Table 1, the counteranion in the borate [expressed as A(H)⁺ in Scheme 1] seems to especially affect the activity rather than the DD incorporation, the M_n value in the resultant copolymers. As reported previously (runs 18 and S44–S47 in Table S2),^{35–37} DD incorporation in toluene was not affected by the cocatalyst system.

On the basis of the copolymerization results with 2M1P and DD, E/VCH copolymerizations by **1** and **3** were conducted in MCH in the presence of **B1**–**B5**. The selected results are summarized in Table 3, and additional results (including the results by **B1**) are shown in Table S3.⁴⁴ It should be noted that the **1**–**B5** catalyst system exhibited much higher catalytic activity than the **1**–MAO catalyst system; the activity reached 152000 kg-polymer/mol-Ti·h under the optimized borate/Ti molar ratio (run 27 in Table 3). Moreover, as observed in the copolymerizations with 2M1P and DD, the VCH contents in the resultant copolymers prepared by the **1**–**B5** catalyst system were high (9.1–9.7 mol %) compared to that prepared by the **1**–MAO catalyst system (6.0 mol %). The activity by **1** was affected by the borate cocatalyst employed, and the VCH content in the copolymer increased upon increasing the VCH concentration charged accompanied with a decrease in both the activity and the M_n values in the resultant copolymers [runs 19 and 20 (**B2**), runs 21 and 22 (**B3**), and runs 25, 28, and 29 (**B5**) in Table 3]. Also note that no significant differences in the VCH contents in the copolymers were observed when these polymerizations by **1**–borate (**B1**–**B5**) catalyst systems were conducted in toluene (Table S3, runs S50–S54).⁴⁴ As demonstrated in the copolymerization with 2M1P,³⁹ the VCH content by the **1**–MAO catalyst system was close to those prepared by the **1**–borate catalyst systems in toluene; the VCH incorporation was thus affected by the solvent (toluene vs MCH). The results thus suggest that the observed difference in MCH would be due to a weak cation–

anion interaction *without* coordination of toluene (and amine or ether, exhibited **A**, as shown in Scheme 1, formed after treatment of **1** with borate) to the assumed cationic alkyl species.^{22,42,43}

It was also revealed that **3**–borate catalyst systems (**B2**–**B4**, runs 31–35 in Table 3) showed better VCH incorporations than the **3**–MAO catalyst system (run 36 in Table 3), whereas the activities by the borate catalyst systems were low compared to that by the **3**–MAO catalyst system. The VCH incorporation seemed somewhat affected by the borate employed (runs 31–35 in Table 3 and runs S57–S59 in Table S3). The resultant copolymers prepared by the **1**–borate and **3**–borate catalyst systems (**B2**–**B5**) possessed high M_n values with unimodal molecular weight distributions ($M_n = 5.63\text{--}11.4 \times 10^4$, $M_w/M_n = 1.65\text{--}2.00$), and their compositions were uniform, as confirmed by DSC thermograms [observed sole melting temperature (by **1**) or glass transition temperature (by **3**), Figures S62–68],⁴⁴ suggesting that the reactions proceed with uniform (single) catalytically active species.

We have shown that conducting the ethylene copolymerizations with DD and VCH by half-titanocenes (**1** and **3**) in the presence of alkane soluble borate cocatalysts (**B2**–**B5**) in MCH enabled efficient syntheses of the copolymers with better comonomer incorporations than those in the presence of MAO cocatalyst in toluene. The activities in MCH were affected by the borate compounds employed. Use of the perfluorinated naphthyl borate, B(C₁₀F₇)₄[−], exhibited higher catalytic activity than the pentafluorophenyl borate, B(C₆F₅)₄[−] (probably due to better delocalization of the counteranion).⁴⁴ Noncoordinating oxonium ion, especially HO⁺(*n*-C₁₄H₂₉)₂·O(*n*-C₁₄H₂₉)₂ (**B5**) containing long alkyl chains, was preferred compared to the ammonium salts (probably due to the poor coordination ability of O(*n*-C₁₄H₂₉)₂ to the assumed cationic species). The information presented here should be helpful not only for the design of an efficient catalyst strategy for synthesis of new copolymers (with sterically encumbered olefins^{38,39} including biobased disubstituted olefin,⁴⁶ low strain cyclic olefins,⁴⁷ etc.) and/or more active catalysts⁴⁸ but also for better understanding of the catalysis mechanism.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsorginorgau.2c00020>.

General experimental procedure, syntheses of Cp*Ti-Me₂(O-2,6-ⁱPr₂-4-SiEt₃C₆H₂) (**3**) and borates [A(H)⁺[B(C₆F₅)₄][−] [A(H)⁺ = N⁺(H)(CH₂CF₃)(*n*-C₁₈H₃₇)₂ (**B2**), HO⁺(*n*-C₁₄H₂₉)₂·O(*n*-C₁₄H₂₉)₂ (**B3**), and HO⁺(*n*-C₁₆H₃₃)₂·O(*n*-C₁₆H₃₃)₂ (**B4**)] or [A(H)⁺[B(C₁₀F₇)₄][−] [A(H)⁺ = HO⁺(*n*-C₁₄H₂₉)₂·O(*n*-C₁₄H₂₉)₂ (**B5**) and N⁺(H)(CH₂CF₃)(*n*-C₁₈H₃₇)₂ (**B6**)], additional results in ethylene copolymerization with 2-methyl-1-pentene, 1-dodecene, and vinylcyclohexane, selected NMR spectra for complex **3**, borates, and the copolymers, selected DSC thermograms of the copolymers, and selected GPC charts of the copolymers (PDF)

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Notes

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(45) A reviewer commented concerning the Al/Ti molar ratios conducted in the copolymerization. As reported previously,^{5–7,24,35–40} a certain amount of Al alkyls was necessary as scavenger (removal of impurities) in addition to a role as the cocatalyst (to avoid the catalyst decomposition by interacting with borate). Therefore, the Al/Ti molar ratios became high in the copolymerizations by the highly active catalysts.

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