

Activator effects in metallocene-based alkene polymerisations: unexpectedly strong dependence of catalyst activity on trityl concentration

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Abstract

The influence of the concentration of $\text{CPh}_3^+\text{B}(\text{C}_6\text{F}_5)_4^-$ as the activator for metallocene polymerisation catalysts has been quantified. Whereas typically a 1:1 molar ratio of activator and metallocene dialkyl is employed, in line with the expected stoichiometry of alkyl abstraction, significant increases in the productivity of some—but not all—propene polymerisation catalysts have been found. The effect is particularly marked for catalysts with more open structures, such as the constrained-geometry complex $(\text{C}_5\text{Me}_4\text{SiMe}_2\text{NBu}^t)\text{TiCl}_2$, where the activity could be increased by about an order of magnitude. Most catalysts show an optimum CPh_3^+/Zr ratio, beyond which further increases of $[\text{CPh}_3^+]$ has no effect. While some zirconocenes reach activities of up to $1.2 \times 10^9 \text{ g PP} (\text{mol Zr})^{-1} [\text{C}_3\text{H}_6]^{-1} \text{ h}^{-1}$ (25 °C, 1 bar), other, typically less active zirconocenes do not show a trityl response at all. Possible reasons for this effect are discussed.

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1. Introduction

The factors controlling the activity of olefin polymerisation catalysts are strongly dependent on reaction conditions and generally poorly understood [1–3]. The advent of catalysts based on cationic metallocenium complexes paired with weakly coordinating anions has however provided the basis for more detailed mechanistic understanding and more rational catalyst design [4–8]. In this context, we have for some time been concerned with the quantification of ligand- and anion effects in metallocene-based propene polymerisation catalysts, such as the intrinsic activity of catalysts extrapolated to zero concentration under a protocol ensuring the absence of mass-transport limitations, and the contribution of the anion to the activation barrier of propene polymerisations [9–12].

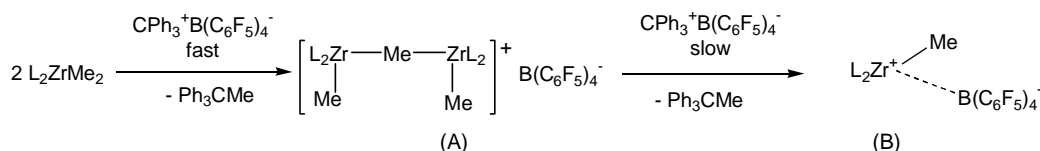
The reaction of group 4 metallocene dialkyls with cation generating agents such as $\text{HNMe}_2\text{Ph}^+\text{B}(\text{C}_6\text{F}_5)_4^-$, $\text{B}(\text{C}_6\text{F}_5)_3$

or $\text{CPh}_3^+\text{B}(\text{C}_6\text{F}_5)_4^-$ to give catalytically active cationic metal alkyl species is well established. In the case of metallocene dimethyls activated with $\text{CPh}_3^+\text{B}(\text{C}_6\text{F}_5)_4^-$ it has been shown that the reaction proceeds in two steps, the fast formation of a methyl-bridged binuclear species **A** followed by the slower reaction with further CPh_3^+ to give the mononuclear ion pairs **B** (Scheme 1) [13,14] and for related $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ complexes see [15].

More convenient systems based on metallocene dichloride precursors, such as $\text{L}_2\text{ZrCl}_2/\text{TIBA}/\text{CPh}_3^+\text{B}(\text{C}_6\text{F}_5)_4^-$ are frequently employed with great success [16]; they are thought to involve a similar reaction sequence, again involving a 1:1 Zr/trityl molar ratio (TIBA = Al^iBu_3). In this case, with TIBA as alkylating agent, the formation of alkyl-bridged binuclear intermediates of type **A** has not been established, and it is thought that the reaction leads directly to mononuclear ion pairs of type **B**. Since TIBA as scavenger and alkylating agent results in very high activities with excellent reproducibility, this activator system has been employed for most of the present study. We report here a comparative study on the dependence of catalyst productivities on the concentration of $\text{CPh}_3^+\text{B}(\text{C}_6\text{F}_5)_4^-$ as

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Scheme 1.

activator in the presence of TIBA. Unexpectedly large activity enhancements were found both under quenched-flow and batch reaction conditions.

2. Experimental part

2.1. Materials

All manipulations were performed under dry nitrogen gas using standard Schlenk techniques. Solvents were purified by distillation under nitrogen from sodium–potassium alloy (light petroleum, bp 40–60 °C) or sodium (low-sulphur toluene) or sodium-benzophenone (THF). Propene (BOC, 99%) was dried by passing through a column packed with supported P₂O₅ with moisture indicator, followed by a column of 4 Å molecular sieves. *rac*-Me₂Si(Ind)₂ZrCl₂ (**1-Cl**) [17], *rac*-Me₂Si(Ind)₂ZrMe₂ (**1-Me**) [18], Me₂C(C₅H₅)(Fluorenyl)ZrCl₂ (**4**) [19], Me₂Si(C₅Me₄)N^tBuTiCl₂ (**5-Cl**) [20], Me₂Si(C₅Me₄)N^tBuTiMe₂ (**5-Me**) [21] and (C₅H₅)₂ZrCl₂ (**6**) and [C₆H₅CH₂NEt₃]-[B(C₆F₅)₄] [12] were prepared according to literature methods and stored as solids in a dry-box under nitrogen at room temperature. *rac*-Me₂Si(2-Me-4,5-Benz(e)Ind)₂ZrCl₂, (**2**) and *rac*-C₂H₄(4,7-Me₂Ind)₂ZrCl₂, (**3**) were kindly donated by Dr. L. Resconi (Basell). [Ph₃C][B(C₆F₅)₄] was synthesized from Ph₃CCl with Li[B(C₆F₅)₄] in dichloromethane and recrystallised from a dichloromethane/light petroleum mixture solvent to afford a yellow crystalline solid in 97% yield [22]. Li[B(C₆F₅)₄] was made from B(C₆F₅)₃ and LiC₆F₅ in light petroleum [23] and was free from other borate impurities within NMR detection limits (¹⁹F, ¹¹B) without further purification.

2.2. Apparatus

NMR (¹H, ¹³C, ¹⁹F, ¹¹B) spectra were recorded on a Bruker Avance DPX300 spectrometer. Chemical shifts were referenced to residual solvent peaks. Curve fitting was carried out using Origin 6.1 Scientific Graphing and Analysis Software. Polymer molecular weights were determined by gel permeation chromatography in 1,2,4-trichlorobenzene with antioxidant at 160 °C, using a Polymer Laboratories GPC-220 instrument equipped with two PL Gel mixed-B columns and a refractive index detector and are measured relative to polystyrene standards. The quenched-flow apparatus was as reported previously [12], with a mixing chamber constructed from glass capillary tubing of 1 mm

i.d., with Luer fittings and a dead volume of 1 μL, corresponding to a dead time of ca. 1 ms (calculated for a typical flow rate of 42 mL min⁻¹). Reaction tubes were stainless steel, 10–19 gauge with lengths of 12–24 in. Batch reactions were conducted in five parallel 400 mL flasks equipped with Teflon stirrer bars, connected via a Schlenk line to the monomer supply. The temperature was controlled by a circulating water bath thermostated at 25 ± 0.1 °C.

2.3. Propene polymerisations

Stock solutions of the catalyst precursor (10⁻³ mol L⁻¹) were made by dissolving a certain amount of precatalyst in the required volume of toluene together with Al^tBu₃ (Al:Zr = 10:1). Since dilute solutions of metallocenes were found to deteriorate over time in spite of stringent precautions, fresh stock solutions were prepared for each set of experiments. Stock solutions of the activator (10⁻³ mol L⁻¹) were made by dissolving a certain amount of [Ph₃C][B(C₆F₅)₄] in the required volume of toluene. All measurements were conducted with metallocene solutions that were less than 2 h old.

2.4. Quenched-flow experiments

Propene solutions were prepared by thermostating 1 L of toluene containing 2 mmol of Al^tBu₃ at 25 ± 0.1 °C under 1 bar of propene for 3 h ([C₃H₆] = 0.62 mol L⁻¹). The propene solution was drawn into a 100 mL gas-tight Hamilton syringe by means of a stepless syringe pump. Flow rates were 40 mL min⁻¹ for the monomer solution and 1 mL min⁻¹ each for catalyst and activator, to give a total flow rate of 42 mL min⁻¹, which was kept constant for this series of experiments. Quenching was achieved by a jet of methanol directed perpendicular to the reactor effluent stream. At the quenching point, the ratio of methanol to toluene was about 1.5:1. The quenched solution was collected in a beaker containing excess methanol. Polymer collection time was 1 min. Reaction times were varied by selecting appropriate tube lengths and diameters. In a typical run the total volume of solution passed was sufficient to produce about 0.01–0.3 g polymer, and the volume of quenched solution was about 200 mL. The polymer was collected by filtration on a no. 4 glass sinter filter, washed with methanol and dried overnight at 100 °C. Each experiment was generally repeated 4–6 times, with a reproducibility of typically ±5%. After each run the reactor tube was cleaned out with hot toluene to remove a thin surface layer of polymer deposit.

2.5. Batch reactions

A battery of five 400 mL flasks was set up in parallel. Each flask was charged with 100 mL of toluene containing 0.15 mmol of Al^tBu_3 and equilibrated under 1 bar of propene for 30 min at 25 °C. The required amount of pre-catalyst and activator solutions were injected at same time using gas-tight Hamilton syringes. At the desired polymerisation time the reactions were terminated by injecting 20 mL of methanol. The polymer was precipitated with 300 mL of acidified methanol, filtered and dried overnight at 100 °C.

Scavenger-free polymerisations with $[(\text{SBI})\text{ZrCH}_2\text{SiMe}_3^+ \cdots \text{B}(\text{C}_6\text{F}_4)_4^-]$ (**7**) were carried out at $[\text{Zr}] = 0.1$ mmol/L. To avoid reaction exotherms, lower zirconocene concentrations were attempted but gave poorly reproducible results. At trityl:Zr ratios of 3:1 mass-transport limitation could not be excluded.

3. Results and discussion

Soluble alkene polymerisation catalysts based on metallocenes activated with $\text{CPh}_3^+\text{B}(\text{C}_6\text{F}_5)_4^-$ typically employ a stoichiometric trityl/metallocene ratio of 1:1, in line with the reaction sequence shown in Scheme 1. As part of our quenched-flow kinetic investigation of the system $(\text{SBI})\text{ZrMe}_2(\text{1-Me})/\text{TIBA}/\text{CPh}_3^+\text{B}(\text{C}_6\text{F}_5)_4^-$ [12] we found, however, that catalyst productivity increases with increasing trityl concentration, up to a trityl/Zr molar ratio of 3:1 (Fig. 1, $\text{SBI} = \text{rac-Me}_2\text{Si}(\text{1-Ind})_2$). Additional aliquots of $\text{CPh}_3^+\text{B}(\text{C}_6\text{F}_5)_4^-$ did not result in further increases in propagation rates and even led to a slight decline in productivity.

Our first assumption was that in view of the short reaction times used for kinetic experiments (0.2–5 s) the activity increase at higher $[\text{CPh}_3^+]$ was a function of improved cat-

alyst activation. This was tested by comparing the proportion of catalytically active species in these reactions. As we showed previously [12], curve fitting of polymer yields Y as a function of reaction time t_R provides the “apparent” propagation rate constant k_p^{app} ; “apparent” since it relies on the assumption that 100% of the precursor complex has become catalytically active. By contrast, the time evolution of the number-average molecular weight $\bar{M}_n(t_R)$ is independent of the active species concentration and gives a constant describing the rate of chain growth, k_p . The ratio k_p^{app}/k_p can be taken as a measure of the fraction of total catalyst added that is actively involved in chain growth at any one time, i.e. the active species concentration $[\text{C}^*]$. This determination of $[\text{C}^*]$ was conducted for the catalysts **1-Cl** and **1-Me** (Table 1), and for comparison also for the “constrained-geometry” titanium catalyst $(\text{C}_5\text{Me}_4\text{SiMe}_2\text{NBu}^t)\text{TiCl}_2$ (**5-Cl**, cf. Scheme 2); data for the latter are collected in Table 2. Kinetic data and $[\text{C}^*]$ for **1-Cl**, **1-Me** and **5-Cl** are given in Table 3.

The results show that while for **1-Cl** there is a tendency towards higher $[\text{C}^*]$ with increasing $[\text{CPh}_3^+]$, from 15 to 22 mol%, the picture is inconsistent, and there is no significant difference for **1-Me**. For this catalyst system at 25 °C, the half-life of initiation had been estimated [12] as $t_{1/2}^{\text{init}} = 0.24 \pm 0.03$ s, to give, at the chosen monomer concentration, an initiation rate $k_i^{\text{obs}} = k_i[\text{M}] = (2.9 \pm 0.4) \text{ s}^{-1}$. In other words, after about four half-lives (ca. 1 s) catalyst initiation should no longer be important. On the other hand, the “constrained-geometry” titanium catalyst $(\text{C}_5\text{Me}_4\text{SiMe}_2\text{NBu}^t)\text{TiCl}_2$ (**5-Cl**, see Scheme 2) shows about a doubling of $[\text{C}^*]$ on increasing $[\text{CPh}_3^+]$ by a factor of 3, to 34 mol%. While this may account for some productivity increases, it is evident that even raising $[\text{C}^*]$ to 100% would not account for the productivity increases observed with this catalysts in batch reactions (see below).

The influence of slow initiation should be unimportant in batch reactions where the reaction times are much longer.

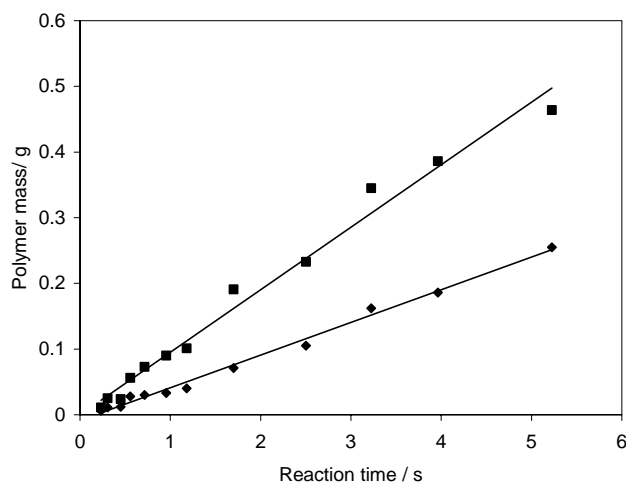
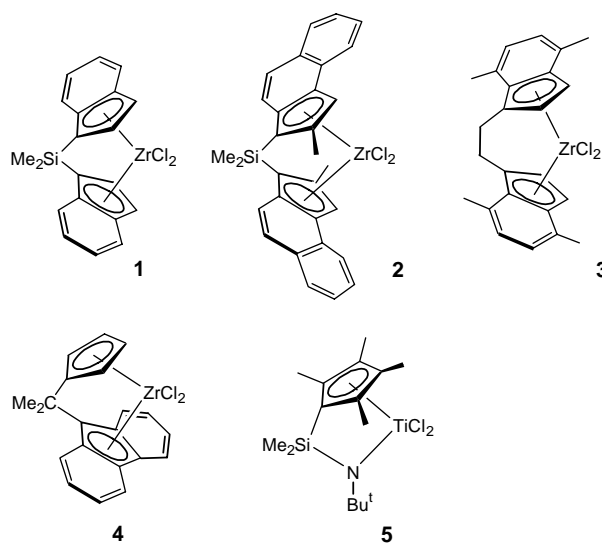


Fig. 1. Quenched-flow data (toluene, 25 °C, $[\text{C}_3\text{H}_6] = 0.59 \text{ mol L}^{-1}$) showing the influence of the $\text{CPh}_3^+\text{B}(\text{C}_6\text{F}_5)_4^-$ concentration on propene polymerisation activities with **1**/TIBA/ $\text{CPh}_3^+\text{B}(\text{C}_6\text{F}_5)_4^-$: (◆) $[\text{Ph}_3\text{C}]/[\text{Zr}] = 1:1$; (■) $[\text{Ph}_3\text{C}]/[\text{Zr}] = 3:1$; $[\text{Zr}] = 4.7 \times 10^{-5} \text{ mol L}^{-1}$.



Scheme 2.

Table 1

Quenched-flow kinetic data for the systems **1**-Cl/AlⁱBu₃/[Ph₃C][B(C₆F₅)₄] and **1**-Me/AlⁱBu₃/[Ph₃C][B(C₆F₅)₄]^a

Time (s)	1 -Cl/Al ⁱ Bu ₃ /[Ph ₃ C][B(C ₆ F ₅) ₄]						1 -Me/Al ⁱ Bu ₃ /[Ph ₃ C][B(C ₆ F ₅) ₄]					
	[Ph ₃ C]/[Zr] = 1:1			[Ph ₃ C]/[Zr] = 3:1			[Ph ₃ C]/[Zr] = 1:1			[Ph ₃ C]/[Zr] = 3:1		
	Yield (g) ^b	[M] (mol L ⁻¹)	M _n ^c	Yield (g) ^b	[M] (mol L ⁻¹)	M _n ^c	Yield (g) ^b	[M] (mol L ⁻¹)	M _n ^c	Yield (g) ^b	[M] (mol L ⁻¹)	M _n ^c
0.234	0.006	0.602	11600	0.011	0.584	13600	0.006	0.602	13000	0.014	0.582	13700
0.307	0.011	0.599	13800	0.025	0.576	16600	0.008	0.601	12900	0.013	0.583	19300
0.451	0.012	0.598	13800	0.024	0.576	17500	0.011	0.599	17500	0.024	0.576	19700
0.557	0.028	0.589	18300	0.056	0.558	23100	0.024	0.591	21100	0.040	0.567	23400
0.716	0.030	0.588	19100	0.073	0.549	22900	0.024	0.592	24700	0.044	0.565	26700
0.955	0.033	0.586	19800	0.090	0.539	24300	0.042	0.582	23300	0.067	0.552	27200
1.182	0.040	0.583	21500	0.101	0.533	26100	0.046	0.579	27900	0.075	0.548	28900
1.700	0.071	0.565	25300	0.191	0.482	28900	0.069	0.566	31600	0.120	0.522	31900
2.502	0.105	0.545	27600	0.233	0.458	30900	0.116	0.539	33900	0.178	0.489	33400
3.225	0.162	0.513	28700	0.345	0.395	30700	0.148	0.521	34300	0.235	0.457	33600
3.964	0.186	0.499	30300	0.386	0.371	32500	0.196	0.494	33900	0.279	0.432	34100
5.226	0.255	0.461	30300	0.464	0.327	30900	0.250	0.463	33700	0.386	0.371	32900

^a Conditions: [Zr] = 4.76 × 10⁻⁵ mol L⁻¹, [M]₀ = 0.59 mol L⁻¹ for [Ph₃C]/[Zr] = 3:1 and [M]₀ = 0.602 mol L⁻¹ for [Ph₃C]/[Zr] = 1:1, T = 25 °C.^b Average of 4–5 experiments with errors less than 6%.^c Average of two determinations.

Table 2

Quenched-flow kinetic data for the constrained-geometry catalyst system **5**-Cl/AlⁱBu₃/[Ph₃C][B(C₆F₅)₄]^a

Time (s)	5 -Cl/Al ⁱ Bu ₃ /[Ph ₃ C][B(C ₆ F ₅) ₄]					
	[Ph ₃ C]/[Ti] = 1:1			[Ph ₃ C]/[Ti] = 3:1		
	Yield (g) ^b	[M] (mol L ⁻¹)	M _n ^c	Yield (g) ^b	[M] (mol L ⁻¹)	M _n ^c
0.234	0.008	0.600	31800	0.043	0.581	58200
0.307	0.020	0.594	37300	0.055	0.574	73700
0.451	0.025	0.591	43100	0.074	0.563	75400
0.557	0.031	0.588	41500	0.069	0.566	76700
0.716	0.035	0.585	46600	0.119	0.538	87600
0.955	0.049	0.577	57300	0.159	0.515	90300
1.182	0.065	0.568	61400	0.167	0.511	103200
1.700	0.067	0.567	72300	0.270	0.452	108100
2.502	0.168	0.510	76400	0.352	0.406	111500
3.225	0.216	0.483	77500	0.498	0.323	129700
3.964	0.247	0.465	87000	0.551	0.292	126400
5.226	0.301	0.434	82600	0.650	0.236	117300

^a [Ti] = 4.76 × 10⁻⁵ mol L⁻¹, [M]₀ = 0.59 mol L⁻¹ for [Ph₃C]/[Ti] = 3:1 and [M]₀ = 0.602 mol L⁻¹ for [Ph₃C]/[Ti] = 1:1, T = 25 °C.^b Average of 4–5 experiments with errors less than 6%.^c Average of two determinations.

Table 3

Rate constants derived from propene polymerisation quenched-flow kinetics with **1** and **5** activated with TIBA/CPh₃⁺B(C₆F₅)₄^{-a}

	Precatalyst					
	1 -Cl		1 -Me		5 -Cl	
	1:1	3:1	1:1	3:1	1:1	3:1
k ^{app} (L mol ⁻¹ s ⁻¹)	1100	2500	1100	1800	2800	7800
k _p (L mol ⁻¹ s ⁻¹)	8800	11200	7400	11000	19300	22300
k ^{app} /k _p	0.13	0.22	0.15	0.16	0.15	0.34

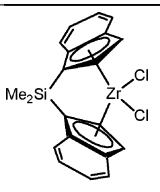
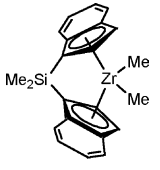
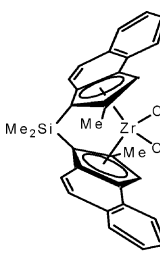
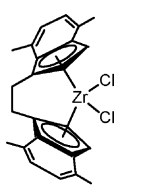
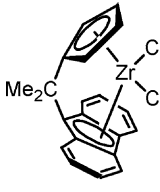
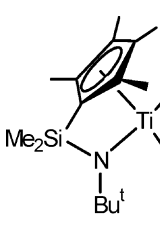
1:1 and 3:1 are the [Ph₃C]/[metal] ratios.^a For conditions see Tables 1 and 2.

This was tested for a representative number of metallocenes, the structures of which are shown in Scheme 2. Results are given in Table 4 and illustrated in Fig. 2. Catalysts **3** and **4**, which have low propene polymerisation activities, show no response to changes in the trityl borate concentration. By contrast, **1** exhibited the same behaviour in batch reactions of 5 min duration as was seen in the quenched-flow experiments of 0.2–5 s: the productivity shows a maximum at a CPh₃⁺/Zr molar ratio of 3:1; the enhanced activity of Me₂Si(2-Me-4-Ph-Ind)₂ZrBz₂ at a CPh₃⁺/Zr ratio of 3:1 has been noted [24]. Within practicable limits this behaviour is independent of the zirconium concentration: although [Zr] in batch reactions was 30 times lower than in the quenched-flow experiments, the optimum trityl/Zr ratio remained unchanged.

Much more pronounced effects are seen for the “constrained-geometry” catalyst **5**: a 10-fold increase in [CPh₃⁺] led to an increase in catalyst productivity by one order of magnitude, from ca. 8.5 × 10⁷ to 8.3 × 10⁸ g PP (mol Ti)⁻¹ [C₃H₆]⁻¹ h⁻¹. Even the high-activity catalyst **2** can be improved by further trityl borate additions, with a productivity increase from 4.5 × 10⁸ at CPh₃⁺/Zr =

Table 4

The effect of trityl borate concentration, expressed as borate/metal ratio, on catalyst productivities in batch reactions^a

Run	Precatalyst formula	Precatalyst (μmol)	Activator (μmol)	[Ph ₃ C]/[metal]	Time (min)	Polymer mass (g)	Productivity ^b	M _n (×10 ⁻⁵)	M _w /M _n
1		0.1	0.1	1:1	5	0.683	132.3		
2		0.1	0.2	2:1	5	1.293	250.0		
3		0.1	0.3	3:1	5	1.583	306.5		
4		0.1	0.4	4:1	5	1.615	312.9		
5		0.1	0.5	5:1	5	1.525	295.2		
	1-Cl								
6		0.3	0.3	1:1	1	0.554	179.0		
7		0.3	0.6	2:1	1	0.718	232.3		
8		0.3	0.9	3:1	1	0.791	254.8		
9		0.3	1.2	4:1	1	0.786	253.2		
	1-Me								
10		0.2	0.2	1:1	0.5	0.471	456.5	2.0	1.9
11		0.2	0.4	2:1	0.5	0.706	683.9	1.5	2.0
12		0.2	0.6	3:1	0.5	0.84	819.4	1.7	1.8
13		0.2	0.8	4:1	0.5	0.954	922.6	1.5	2.2
14		0.2	1.0	5:1	0.5	1.270	1229.0	1.4	1.9
15		0.2	1.4	7:1	0.5	1.217	1177.0	1.5	1.8
16		0.2	2.0	10:1	0.5	1.226	1187.0	1.5	2.0
17		0.2	3.0	15:1	0.5	1.242	1202.0		
	2								
18		0.4	0.4	1:1	5	0.160	7.7	0.08	2.1
19		0.4	0.8	2:1	5	0.190	7.7	0.09	1.9
20		0.4	1.2	3:1	5	0.177	9.2	0.08	2.1
21		0.4	1.6	4:1	5	0.183	8.5	0.08	2.1
21		0.4	2.0	5:1	5	0.160	8.9	0.08	2.1
	3								
23		1	1	1:1	1	0.361	35.0		
24		1	2	2:1	1	0.430	42.4		
25		1	3	3:1	1	0.433	41.9		
26		1	4	4:1	1	0.457	44.2		
	4								
27		0.1	0.1	1:1	4	0.356	85.5	2.8	1.8
28		0.1	0.2	2:1	4	0.773	187.1	1.9	2.4
29		0.1	0.3	3:1	4	1.326	321.0	2.3	2.1
30		0.1	0.4	4:1	4	1.531	371.0	2.2	2.1
31		0.1	0.5	5:1	4	1.922	464.5	2.4	2.0
32		0.1	0.7	7:1	4	2.840	687.1	2.0	2.1
33		0.1	1.0	10:1	4	3.242	783.9	1.7	2.4
34		0.02	0.2	10:1	5	0.836	809.7		
35		0.2	2.0	10:1	1	1.732	835.5		
36		5-Cl	0.02	0.4	20:1	5	0.803	777.4	
37		0.02	1.0	50:1	5	0.711	688.7		

^a Batch reactions in 100 mL of toluene with Al^tBu₃, [Al] = 10⁻³ mol L⁻¹, at 25 °C. Precatalyst stock solutions prepared in toluene containing Al^tBu₃, [Al]/[metal] ratio 10:1.

^b Productivity in 10⁶ g PP (mol catalyst)⁻¹ h⁻¹ [C₃H₆]⁻¹.

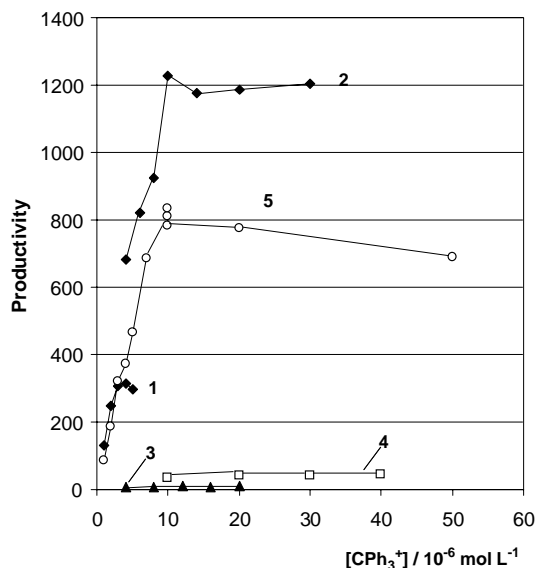


Fig. 2. Dependence of propene polymerisation activity of various metallocene catalysts on the $\text{CPh}_3^+\text{B}(\text{C}_6\text{F}_4)_4^-$ concentration at $25^\circ\text{C}/1\text{ bar}$ (metal/TIBA = 1:100, toluene, $[\text{Al}] = 10^{-3}\text{ mol L}^{-1}$; $[\text{C}_3\text{H}_6] = 0.62\text{ mol L}^{-1}$). [Metalocene] = lowest $[\text{CPh}_3^+]$ data point in each series. Productivity in $10^6\text{ g PP}(\text{mol metal})^{-1}\text{ h}^{-1}[\text{C}_3\text{H}_6]^{-1}$.

1:1 to almost $1.2 \times 10^9\text{ g PP}(\text{mol Zr})^{-1}[\text{C}_3\text{H}_6]^{-1}\text{ h}^{-1}$ at $\text{CPh}_3^+/\text{Zr} \approx 5:1$.

It should be noted that although chloride-containing systems have been reported to be less active than chloride-free analogues [25], this is not borne out here in the case of higher trityl concentrations. Thus while 1-Cl/TIBA/ $\text{CPh}_3^+\text{B}(\text{C}_6\text{F}_4)_4^-$ at $\text{CPh}_3^+/\text{Zr} = 1:1$ is indeed

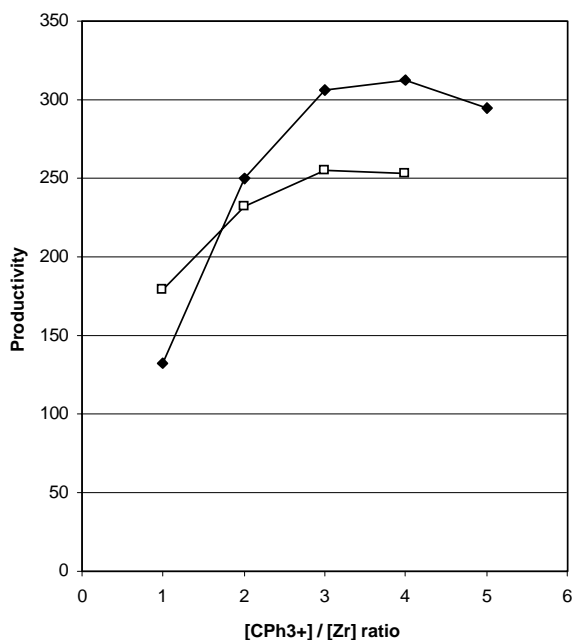


Fig. 3. Comparison of propene polymerisation productivities of $(\text{SBI})\text{ZrX}_2/\text{TIBA}/\text{CPh}_3^+\text{B}(\text{C}_6\text{F}_5)_4^-$ for $\text{X} = \text{Me}$ (\square) and $\text{X} = \text{Cl}$ (\blacklozenge) (batch reactions, 25°C , 0.5 min). Productivity in $10^6\text{ g PP}(\text{mol Zr})^{-1}\text{ h}^{-1}[\text{C}_3\text{H}_6]^{-1}$.

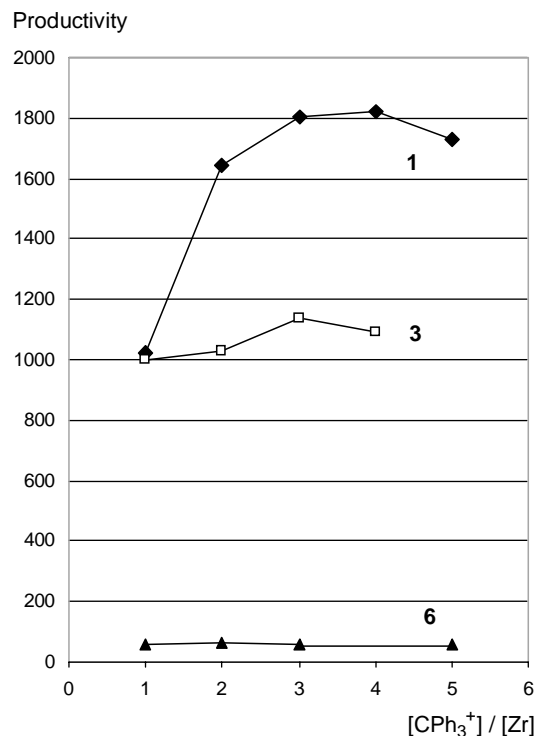


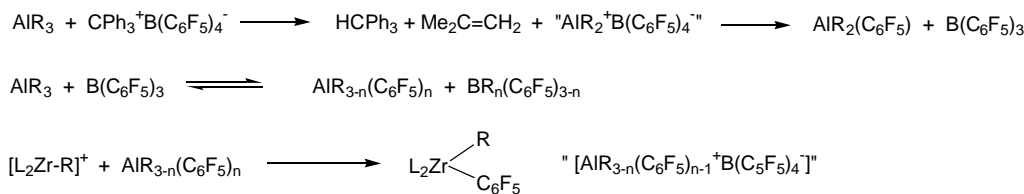
Fig. 4. Effect of trityl concentration on ethene polymerisation activities of zirconocene catalysts (25°C , 1 bar, $t_R = 0.5\text{ min}$). 1: $[\text{Zr}] = 0.5 \times 10^{-6}\text{ M}$; 3: $[\text{Zr}] = 1 \times 10^{-6}\text{ M}$; 6: $[\text{Zr}] = 1 \times 10^{-6}\text{ M}$. Productivity in $10^6\text{ g PE}(\text{mol Zr})^{-1}\text{ bar}^{-1}\text{ h}^{-1}$.

less active than the 1-Me analogue, at higher CPh_3^+/Zr molar ratios the converse was found (Fig. 3). The effect is not dramatic but reproducible. The reasons for this behaviour are not clear at present.

A similar effect with rising $[\text{CPh}_3^+]$ was seen in ethylene polymerisations catalysed by 1, although the lower monomer concentration and the associated danger of mass-transport limitation, as well as the tendency for early polymer precipitation make these productivities more difficult to quantify under our low-pressure conditions. However, the data for 1 gain credence by the observation that neither the high-yielding catalyst 3 nor Cp_2ZrCl_2 (6) as a comparatively less active catalyst showed a significant $[\text{CPh}_3^+]$ response (Fig. 4).

The origin of the “trityl effect” is uncertain. In fact, the opposite effect might have been expected: It is known that excess trityl tetraarylborate reacts with TIBA over a period of minutes with decomposition and formation of neutral aluminum- C_6F_5 products (Scheme 3) which, on reaction with zirconocenes, are a source of catalyst deactivation [26].

In principle, another possibility might be the formation of ion aggregates that react slightly faster than mononuclear ion pairs. For example, such aggregates might take the form $[\text{L}_2\text{ZrR}]^+[\text{X}^- \cdots \text{CPh}_3^+ \cdots \text{X}^-]$. Ion aggregates have first been discussed by Brintzinger and co-workers [3a,27]. On the other hand, the addition of other salts such as $[\text{PhCH}_2\text{NEt}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ up to borate/Zr ratios of 20:1



Scheme 3.

Table 5

Propene polymerisations with [(SBI)ZrCH₂SiMe₃⁺⋯B(C₆F₅)₄⁻] (**7**) in the absence of TIBA^a

Zr (μmol)	CPh ₃ ⁺ (μmol)	t _R (min)	PP yield (g)	Productivity ^b
10	10	0.5	3.766 ± 0.05	63.6 ± 0.9
10	30	0.5	5.030	85.1

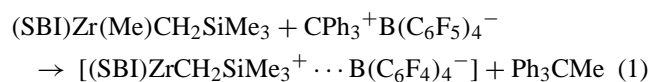
^a Conditions: T = 20 °C, [C₃H₆] = 0.71 mol L⁻¹, 100 mL toluene.

^b In 10⁶ g PP (mol Zr)⁻¹ h⁻¹ [C₃H₆]⁻¹.

do not show any effect on catalyst productivity [12], and the facile reaction of CPh₃⁺ with TIBA outlined above make the persistence of such aggregates unlikely.

The possibility that the effect might be connected with the reaction of metallocenes with TIBA had to be considered. Zirconocenes react with excess TIBA in toluene to give a complex mixture of hydride and aluminohydride species, at least in the absence of olefin monomer [28]. At this stage we feel it cannot be excluded that, for example, μ-H species are formed which require higher concentrations of CPh₃⁺ for effective transformation into active mononuclear species, i.e. the effect may be due to processes commensurate with the timescale of the polymerisation experiments. The intermediate formation of hydrido-bridged species might indeed account for the different response of different metallocenes to changes in trityl activator concentration. This mechanistic possibility awaits confirmation by kinetic data on CPh₃⁺/metallocene reactions.

In order to exclude the presence of TIBA, the new ion pair [(SBI)ZrCH₂SiMe₃⁺⋯B(C₆F₄)₄⁻] (**7**) was selectively synthesized according to the following equation [29]:



Compound **7** is stable for days in toluene solution at ambient temperature and does not require TIBA as a co-activator or scavenger. Here, too, increasing the trityl/Zr ratio from 1:1 to 3:1 results in a 33% increase in the propene polymerisation activity (Table 5). In this case the reaction at trityl/Zr = 3:1 was noticeably more vigorous than at 1:1. Since attempts to reduce [Zr] below 10 μmol often led to complete catalyst deactivation by impurities at comparable background concentrations,¹ the productivities (Table 5) are

¹ Scavenger-free propene polymerisations with (SBI)Zr(Me)CH₂-SiMe₃/B(C₆F₅)₃ suggested that ca. 70% of catalyst is deactivated by impurities, cf. [29].

likely to be affected by mass-transport limitation and represent lower limit estimates.

4. Conclusion

Metallocene-based alkene polymerisation catalysts show a variable response to the activator CPh₃⁺B(C₆F₅)₄⁻, and increasing the activator concentration beyond the 1:1 molar ratio expected on the basis of the activation mechanism outlined in Scheme 1 can lead to higher catalyst productivities in some—but not all—catalysts. In the case of the most active zirconocene complex **2**, very high productivities were observed even under only 1 bar monomer at room temperature, up to ca. 1.2 × 10⁹ g PP (mol Zr)⁻¹ [C₃H₆]⁻¹ h⁻¹. The effect depends on ligand structure and is absent in lower activity catalysts. By contrast, the more open “constrained-geometry” titanium system showed a particularly large enhancement of catalyst productivity, by one order of magnitude. More detailed kinetic investigations of this aspect of catalyst activation are in progress.

Acknowledgements

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