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Substituent Effects on Titanocenium Catalysts

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Titanocene dichloride (1) and its bis(trifluoromethyl) (2) and bis(*N*,*N*-dimethylamino) (3) derivatives have been compared as catalysts for ethylene and propylene polymerizations using both methylaluminoxane (MAO) and triphenylcarbenium tetrakis(pentafluorophenyl)borate (4)/tri-isobutylaluminum (TIBA) as cocatalysts. The differences between the activities of the three 'free' titanocenium ions and the $\bar{M}_w$ of the polyolefins produced by them may be attributable to the relative stabilities of the intermediate olefin–titanocenium π-complexes. Interaction of either the neutral MAO or its anion with the titanocenium species may be responsible for the significantly lower catalytic efficiencies when the precursors were activated by MAO than by the 4/TIBA system.

Keywords: Titanocenium, olefin polymerizations, Ziegler–Natta catalysis

INTRODUCTION

The first homogeneous Ziegler–Natta catalyst Cp_2TiCl_2[1,2] (1; Cp = η^5-cyclopentadienyl) activated with alkylaluminum chlorides exhibited low polymerization activity for ethylene and none for propylene. The use of methylaluminoxane (MAO) as a cocatalyst raised the catalytic activity (*A*) by several orders of magnitude.[3,4] Methyl substitution on Cp rings tends to increase *A*, but permethylated derivatives have low *A*.[5,6] The former was thought to be an electronic effect, whereas a steric effect probably dominates in the latter case. We have found that $AcCpTiCl_3$/MAO and $(AcCp)_2TiCl_2$/MAO have lower *A* than the Cp_2TiCl_2/MAO system (R. H. Grubbs and J. C. W. Chien, unpublished results). The purpose of the present study is to synthesize 1,1′-bis(trifluoromethyl)- (2) and 1,1′-bis(*N*,*N*-dimethylamino)- (3) titanocene dichloride and to compare their olefin polymerization behavior in order to learn more about the electronic effects in Ziegler–Natta catalysis. Trifluoromethyl and *N*,*N*-dimethylamino groups are considered as strongly electron-withdrawing[7] and -donating[8] substituents, respectively. MAO and triphenylcarbenium tetrakis(pentafluorophenyl)borate (4)/tri-isobutylaluminum (TIBA)[9–11] were investigated as the cocatalysts.

EXPERIMENTAL

All operations were carried out under an argon atmosphere using Schlenk and glovebox techniques except where specified. Argon was deoxygenated with activated BTS catalyst and dried with molecular sieves and P_2O_5. Pentane, toluene, tetrahydrofuran and diethyl ether were distilled under argon from sodium–potassium alloy. Methylene chloride was distilled under argon from CaH_2. The compounds Cp_2TiCl_2 and $TiCl_4$ were obtained from Aldrich; the latter was distilled from copper wire. $TlCpCF_3$[7] and $[C_5H_4N(CH_3)_2]_2TiCl_2$[8] (3) were prepared by literature procedures.

1,1′-Bis(trifluoromethyl)titanocene dichloride (2)

Into a 100 cm^3 round-bottom Schlenk flask was placed 40 cm^3 of toluene. The flask was cooled to −20 °C, 1.39 g (4.12 mmol) of $TlCpCF_3$ was added, and the suspension was vigorously stirred. $TiCl_4$ (0.40 g, 2.10 mmol) was added dropwise, the reaction mixture was allowed to warm to room temperature, and stirring was continued for 15 h. The volatiles were removed under vacuum and the residue was extracted with methylene chloride in a Soxhlet apparatus. The extract was passed through a Celite plug and concentrated. The title compound 2 was crystallized at −15 °C as red–orange crystals (0.51 g, 63% yield). Elemental analysis: Calcd for $C_{12}H_8Cl_2F_6Ti$:

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Table 1 Variation of ethylene polymerization activity with $[MAO]/[Cp_2TiCl_2]$ ratio[a]

$Al/Ti \times 10^{-3}$	T_p (°C)	Time (min)	Yield (g)	$A_E \times 10^{-7}$ {g PE $(mol\ Ti)^{-1}\ [C_2H_4]^{-1}\ h^{-1}$}
1	20	10	0.030	0.1
2	20	10	0.246	0.8
3	20	10	0.472	1.53
4	20	10	0.485	1.57
5	20	10	0.533	1.72
6	20	10	0.498	1.61
0.25	0	2.5	0.346	3.9
0.5	0	1.5	0.298	5.5
1	0	0.5	0.400	22.3
2	0	0.5	0.425	28.4
3	0	0.3	0.323	27.0
4	0	0.3	0.292	24.4

[a] $[Cp_2TiCl_2]$ was 10 μM in toluene.

C, 37.44; H, 2.10. Found: C, 37.55; H 2.07%. ^1H NMR (d_8-THF): δ 6.70 (t, 4H, $J = 2.7$ Hz), 7.14 (t, 4H, $J = 2.7$ Hz). ^{19}F NMR (d_8-THF): δ 8.55 (s, CF_3).

Polymerizations

Polymerizations of ethylene and propylene were carried out in 250 cm^3 crown-capped glass pressure reactors containing 50 cm^3 of toluene saturated with the monomer at 15 psig (103 kPa). For MAO-catalyzed polymerizations, an excess amount of MAO was introduced first into the reactor, followed by the titanocene precursor. The reactions formed *in situ* the titanocenium ion together with an anion of MAO. Polymerizations were also catalyzed by 'free' or 'bare' titanocenium intermediates. These were generated by adding TIBA first to the toluene solution of monomer, followed by the titanocene compound and finally **4**.[9–11] The quantity of TIBA corresponds to that needed to scavenge the impurities as well as for alkylation; it was reached by trial and error. Polymerizations were quenched with methanol containing 1 vol.% HCl and the polymer was worked up as described previously.[12,13]

Analysis

^1H and ^{19}F NMR spectra were recorded on a Varian XL-300 spectrometer. ^1H chemical shifts are referenced to residual protons of the solvent. ^{19}F chemical shifts are referenced to $F_2BrCCBrH_2$ as an external standard. Microanalysis was performed by the Microanalytical Laboratory of the University of Massachusetts, Amherst, MA, USA.

RESULTS

The activities of ethylene polymerizations catalyzed by the titanocene/MAO systems can be dependent upon the ratio of the catalyst components. Tables 1 and 2 summarize the results for the polymerizations catalyzed by **1**/MAO and **2**/MAO at 0 °C and 20 °C. The ethylene polymerization activities (A_E) are expressed in the unit g PE $(mol\ Ti)^{-1}\ [C_2H_4]^{-1}\ h^{-1}$.

The A_E of **1**/MAO increases with the increase of Al/Ti ratio to a maximum value of 1.72×10^7 at Al/Ti = 5000 and $T_p = 20$ °C. The catalyst becomes more active at lower temperature; the A_E is about 20-fold greater at $T_p = 0$ °C. The optimum A_E value of 2.8×10^8 was obtained using an Al/Ti = 2000 ratio at 0 °C. The A_E of **2**/MAO is virtually independent of the Al/Ti ratio; it is $(1.1 \pm 0.04) \times 10^6$ and $(5.9 \pm 0.85) \times 10^5$ g PE $(mol\ Ti)^{-1}\ [C_2H_4]^{-1}\ h^{-1}$ at $T_p = 20$ °C and 0 °C, respectively, over the range of Al/Ti ratio from 1000 to 6000. The decrease of A_E with lowering of T_p in this case is contrary to the behavior exhibited by **1**/MAO. A_E for **3**/MAO is also insensitive to the catalyst composition. Table 3 contains the maximum A_E values obtained at the optimum Al/Ti ratio for the three catalyst systems at two T_p values. The catalytic activity decreases in the order **1**/MAO ≫ **2**/MAO ≫ **3**/MAO. As is often the case in Ziegler–Natta catalysis, the molecular

Table 2 Variation of ethylene polymerization activity with $[MAO]/[(CpCF_3)_2TiCl_2]$ ratio[a]

$Al/Ti \times 10^{-3}$	T_p(°C)	Time (min)	Yield (g)	$A_E \times 10^{-7}$ {g PE (mol Ti)$^{-1}$ [C_2H_4]$^{-1}$ h^{-1}}
1	20	10	0.036	0.115
2	20	10	0.034	0.114
3	20	10	0.034	0.110
4	20	10	0.032	0.104
5	20	10	0.035	0.114
6	20	10	0.034	0.110
1	0	15	0.038	0.071
2	0	15	0.033	0.061
3	0	15	0.025	0.046
4	0	15	0.031	0.058
5	0	15	0.034	0.064
6	0	15	0.029	0.055

[a] $[(CpCF_3)_2TiCl_2]$ was 10 μM in toluene.

weight of the polyethylene varies in the opposite order compared with the variation of polymerization activity.

Titanocenium ion was produced by using **4** as the cation-forming agent. The counter-ion is essentially inert and noncoordinating.[9–11, 14–20] Thus the 'free' cation is expected to have the maximum activity for a given precursor compound. Table 4 shows that $\mathbf{1}^+$ is about 14 times more active than **1**/MAO at $T_p = 20$ °C. They have about the same A_E at 0 °C. Bigger differences were seen for the other derivatives. The A_E values for $\mathbf{2}^+$ are about 60 and 80 times greater than **2**/MAO at T_p of 20 °C and 0 °C, respectively. The $\mathbf{3}^+$ catalyst has the lowest A_E of the three titanocenes compared in this work. It is only one-tenth as active as $\mathbf{1}^+$ and has one-quarter the A_E of $\mathbf{2}^+$ at 20 °C. Furthermore, the activity of $\mathbf{3}^+$ suffers great losses with the decrease of T_p. The **3**/MAO system exhibits negligible ethylene polymerization activity.

The polyethylenes produced by $\mathbf{1}^+$ and **1**/MAO have comparable molecular weights. On the other hand, $\mathbf{2}^+$ formed much higher-molecular-weight polyethylene than **2**/MAO. The converse is true for **3**; the 'free' $\mathbf{3}^+$ gives much lower-molecular-weight polymer than **3** activated with MAO.

Cations $\mathbf{1}^+$ and $\mathbf{2}^+$ also polymerized propylene to amorphous polymers; the former is more active but produced lower-$\bar{M}_w$ polymer than the latter (Table 5). Cation $\mathbf{3}^+$ is totally inactive toward propylene. The activity for propylene polymerization (A_p) is about 10^3-fold smaller than A_E for the same cation. The molecular weight of the propylene is only about one-tenth of the molecular weight for the corresponding polyethylene (compare last columns in Tables 4 and 5).

Many attempts were made to polymerize propylene using the titanocene compounds **1**, **2** and **3** activated with MAO. No polymerization was observed even using a high [Ti] = 40 μM and [A]/[Ti] ratios of 1000–6000 at $T_p = 0$ °C or 20 °C.

Table 3 Ethylene polymerization catalyzed with titanocene/MAO

Titanocene Compd	 Concn (μM)	MAO Al/Ti	T_p (°C)	Time (min)	Yield (g)	Activity[a] $A \times 10^{-7}$	Mol. wt,[b] $\bar{M}_w \times 10^{-5}$
1	10	5000	20	10	0.533	1.72	1.15
1	10	2000	0	0.5	0.425	28.4	1.39
2	10	2000	20	10	0.035	0.114	2.52
2	10	1000	0	15	0.038	0.071	4.07
3	10	3000	20	—	—	0.002	8.26
3	20	4000	0	—	—	0.001	7.72

[a] A = activity in g polymer (mol Ti)$^{-1}$ [CH_2H_4]$^{-1}$ h^{-1}. [b] M_w by intrinsic viscosity method.[26]

Table 4 Ethylene polymerization catalyzed with 'bare' cation

Titanocene Compd	Titanocene Concn (μM)	T_p (°C)	TIBA (mm)	Time (min)	Yield (g)	Activity,[a] $A \times 10^{-7}$	Mol. wt,[b] $M_w \times 10^{-5}$
1[c]	10	20	1.0	0.5	0.362	2.34	1.89
1	10	0	2.0	0.5	0.551	3.07	3.90
1	10	−20	2.0	0.5	0.505	2.48	4.71
2[c]	10	20	1.5	1.0	0.223	0.72	6.71
2	10	0	2.0	1.0	0.211	0.59	11.85
2	10	−20	2.0	1.0	0.142	0.35	14.13
3[c]	10	20	1.0	1.0	0.086	0.278	0.894
3	35	0	1.85	10	0.070	0.0049	0.623
3	70	−20	2.6	15	0.036	0.00074	0.226

[a, b] As in Table 3, [c] Concentration of cocatalyst **4** is identical to [Ti].

DISCUSSION OF RESULTS

The catalytic activity of the titanocenes **1** to **3** for ethylene polymerization is related to the rate of polymerization (R_p) by

$$R_p = A_E/28 \times 3600\ \mathrm{M\ s^{-1}} \qquad [1]$$

In the case of the production of zirconocenium ion by **4** and AlR_3, we have shown[10] the process to be very rapid and complete within minutes, even at −20 °C. Since the A_E of $\mathbf{1}^+$ catalyst is comparable with that of zirconocenium species, one can assume similar rapid and complete reactions:

$$Cp_2TiCl_2 + 2AlR_3 \rightarrow [Cp_2TiR_2] + 2AlR_2Cl \qquad [2]$$

$$[Cp_2TiR_2] + Ph_3C^+B^-(C_6F_5)_4 \rightarrow Cp_2Ti^+R + B^-(C_6F_5)_4 + Ph_3CR \qquad [3]$$

Since the $B^-(C_6F_5)_4$ ion is known to be inert and noncoordinating,[9–11, 14–20] and there is no strong Coulombic interaction between Cp_2Ti^+R and $B^-(C_6F_5)_4$, the propagation species is the 'free' titanocenium ion. The propagation step in Ziegler–Natta catalysis comprises olefin π-complexation followed by migratory *cis* insertion:

$$\underset{(C^*)}{Ti^+{-}P_n} + \underset{(M)}{M} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{(C^*M)}{[\pi{-}M \rightarrow Ti^+{-}P_n]} \xrightarrow{k_2} \underset{(C^*)}{Ti^+{-}P_{n+1}} \qquad [4]$$

Attempts in the past to detect C*M were unsuccessful. For instance, Fink *et al.*[21] could not observe any resonance attributable to the cation–ethylene π-complex in the system $Cp_2TiMeCl/AlMeCl_2/C_2H_4$ at 10 °C.

We have recently obtained kinetic evidence which is consistent with olefin π-complexation.[10] Propylene polymerizations were performed over a broad T_p of −60 to +60 °C. The data were

Table 5 Propylene polymerization catalyzed with 'bare' cation[a]

Titanocene	TIBA (mM)	T_p (°C)	Time (min)	Yield (g)	Activity,[a] $A \times 10^{-5}$	Mol wt,[b] $\bar{M}_w \times 10^{-4}$
1[c]	1.5	20	10	0.084	3.03	0.20
1	2.0	0	10	0.113	3.00	3.59
1	3.0	−20	10	0.600	12.7	7.95
2[c]	1.5	20	20	0.040	0.72	7.50
2	2.0	0	20	0.104	1.39	11.12
2	3.0	−20	20	0.050	0.53	11.27
3[c]	3.0	20	30	—	0	—
3	1.0–3.0	0	30	—	0	—
3	1.0–3.0	−20	30	—	0	—

[a, b] As in Table III. [c] Concentration of cocatalyst **4** = [titanocene] = 50 μM.

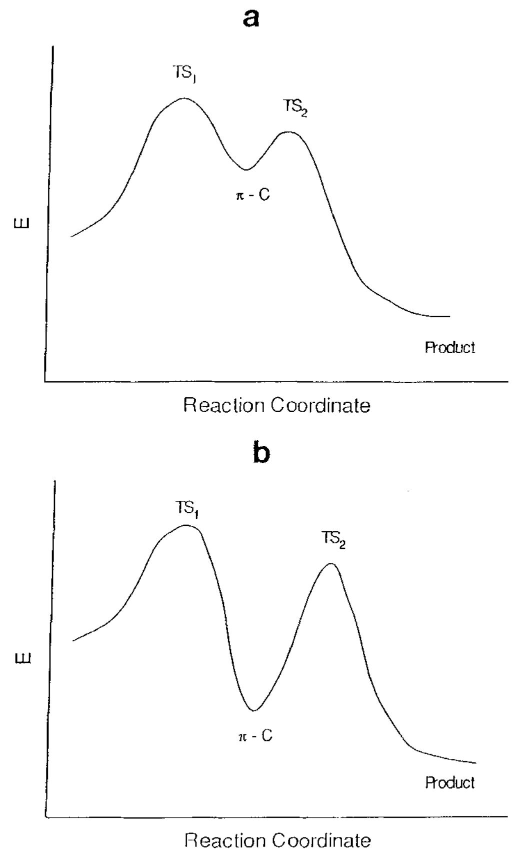


Figure 1 Schematic representation of reaction path from first transition state (TS_1) via π-complex (π-C) and second transition state (TS_2) to monomer insertion: (a) weak π-complex; (b) strong π-complex.

analyzed according to

$$R_p = -\frac{d[M]}{dt} = \frac{k_1 k_2 [C^*]_0 [M]_0}{k_{-1} + k_2 + k_1 [M]_0} \qquad [5]$$

which is analogous to the Michaelis–Menten equation for single-substrate single-enzyme complex kinetics. The stability of C*M governs the dependence of R_p and A on T_p. If the increase of T_p causes the dissociation of C*M, then the catalytic activity would decrease. The opposite variation would be observed if C*M is stable, i.e. at low T_p, there will be a positive A–T_p dependence because of the activation energy required for monomer insertion.

The data for 1^+ and 2^+ in Table 4 showed only a small effect of T_p on A. This indicates that the activation energy for propagation is comparable with the enthalpy of dissociation for $Cp_2Ti^+(M)R$ in Eqn [4] as shown in Fig. 1(a).

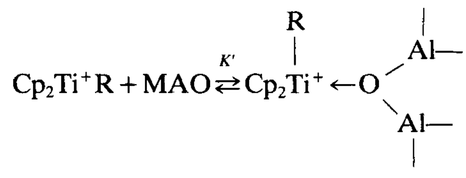
The values of k_2k_1/k_{-1} for 1^+ at 20 °C is $2.3 \times 10^3\ M^{-1}\ s^{-1}$. This is comparable with the results found for several *ansa*-zirconocenium catalysts.[13] A lower value of $k_2k_1/k_{-1} \simeq 700\ M^{-1}\ s^{-1}$ was found for 2^+. The effect of the CF_3 substituent is to withdraw electron density from the Cp ring. This effect could decrease the back-donation from the titanium to the olefin and destabilize the π-complex. The CF_3 substituent may also exert a steric and/or electronic influence to lower the rate constant of propagation. The combined effect of CF_3 is about three-fold lowering of A_E.

The A_E of 3^+ in ethylene polymerization is eight-fold smaller than that of 1^+ at 20 °C (Table 4). This difference increased to 630-fold at 0 °C and >3000-fold at −20 °C. One interpretation of this result is that the π-complex is too stable because the electron-donating dimethylamino group enhances the back-donation of d_π electron density to the π*-orbital of the monomer. Figure 1(b) illustrates the difference of a strong π-complex from a weak one (Fig. 1a). According to this analysis, the large temperature dependence of this system is probably due to the activation energy for k_2 of Eqn [5]. Another possible explanation is that the strong Lewis base Me_2N group can complex strongly with titanocenium to inhibit the latter's ability to catalyze olefin polymerization. This interaction would be favored for the bare 3^+ species, and not as probable for the 3/MAO system because MAO could form a Lewis acid/base complex with the Me_2N group. This is contrary to the negligible A_E found with 3/MAO (Table 3).

The next reaction of titanocene with MAO is the formation of titanocenium ion:[22]

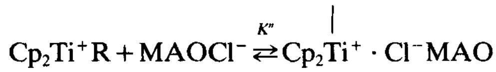
$$Cp_2TiCl_2 + MAO \rightarrow Cp_2Ti^+Me + MAOCl^- \qquad [6]$$

The titanocenium ion would be associated either with a neutral MAO,



$$Cp_2Ti^+R + MAO \overset{K'}{\rightleftarrows} Cp_2\overset{R}{\overset{|}{Ti^+}} \leftarrow O\begin{matrix} \diagup Al— \\ \diagdown Al— \end{matrix} \qquad [7]$$

or with the counter-ion,



$$Cp_2Ti^+R + MAOCl^- \overset{K''}{\rightleftarrows} Cp_2\overset{R}{\overset{|}{Ti^+}} \cdot Cl^-MAO \qquad [8]$$

The former has been demonstrated by the addition of MAO to a propylene polymerization catalyzed by a 'free' zirconocenium system generated by Eqns [2] and [3],[10, 11] which caused an immediate and precipitous drop of R_p. According to this interpretation, the polymerization activity of titanocene/MAO is proportional to the fraction (f) of 'free' titanocenium ions present in the system,

$$f=\frac{[Cp_2Ti^+R]}{[Cp_2Ti^+R]+[Cp_2Ti^+R\cdot Cl^-MAO]+[Cp_2Ti^+R\cdot MAO]}=[Cp_2Ti^+R]/[Ti_0] \qquad [9]$$

It has been established that in metallocenium olefin polymerizations the macromolecular chain length is limited by β-hydride elimination. This elimination is promoted by an electrophilic transition-metal center. One would have expected the $\bar{M}_w$ of the polyethylene to decrease in the order $\mathbf{3}^+>\mathbf{1}^+>\mathbf{2}^+$. However, the opposite order of $\mathbf{2}^+>\mathbf{1}^+>\mathbf{3}^+$ was observed (Table 4). This observation can be rationalized by consideration of the stereoelectronic effects on the transition state for β-hydride elimination. This transition state must have a geometry involving a copolanar arrangement for the titanium atom and the C_α, C_β and H_β atoms of the propagating chain. Therefore, this elimination is easier for the titanocenium ion without π-complexed olefin than for one with π-complexed olefin. A corollary is that the latter needs to undergo olefin dissociation prior to β-hydride elimination:

$$Cp_2Ti^+(M)CH_2CH_2P \overset{K^{-1}}{\rightleftarrows} Cp_2Ti^+CH_2CH_2P+M \qquad [10]$$

$$Cp_2Ti^+CH_2CH_2P \rightarrow Cp_2Ti^+H+CH_2{=}CHP \qquad [11]$$

Furthermore, the net electron donation from the olefin to titanium in the $Cp_2Ti^+(M)P$ species would increase the electron density on the titanium atom and lower its propensity to extract a hydride ion. Finally, as was discussed above, the stability of the π-complex increases in the order $\mathbf{2}^+<\mathbf{1}^+<\mathbf{3}^+$ and $\bar{M}_w$ should follow this order.

The titanocenium catalysts **1–3** have very low activity for propylene polymerization. Comparison of Tables 5 and 4 showed that it is about 1000 times lower than the corresponding activity for ethylene polymerization. Reductions of this magnitude would render $\mathbf{3}^+$ without activity for propylene polymerization, nor would there be any noticeable polymerization by MAO activation. As far as the 'free' titanocenium ions $\mathbf{1}^+$ and $\mathbf{2}^+$ are concerned, their behavior toward propylene polymerization parallels that for ethylene polymerization. The A_p is greater for $\mathbf{1}^+$ than $\mathbf{2}^+$, but the latter produced polypropylene with higher $\bar{M}_w$ than the former.

The differences in the A values for propylene and ethylene are probably not attributable to a greater propylene propagation activation energy. The catalytic activity of $\mathbf{1}^+$ toward the two monomers has comparable dependence on T_p. Another explanation may be the lower stability of the titanocenium–propylene π-complex. However, we have found very similar polymerization activities for the two monomers by various *ansa*-zirconocenium catalysts.[9–11, 23, 24]

There seems to be a basic difference between the titanocene and zirconocene catalysts in the polymerizations of ethylene and α-olefins. A possible cause is the ease of reduction and deactivation of titanocenium alkyls:[25]

$$\begin{aligned}&Ti^+(IV){-}CH_2{-}CH_2{-}P\\&\quad+Ti^+(IV){-}CH_2{-}CH_2{-}P'\\&\quad\rightarrow 2Ti^+(III)+CH_2{=}CH{-}P\\&\quad+CH_3{-}CH_2{-}P'\end{aligned} \qquad [12]$$

$$\begin{aligned}&Ti^+(IV){-}CH_2{-}CH(CH_3){-}P\\&\quad+Ti^+(IV){-}CH_2{-}CH(CH_3){-}P'\\&\quad\rightarrow 2Ti^+(III)+CH_2{=}C(CH_3){-}P\\&\quad+CH_3{-}CH(CH_3){-}P'\end{aligned} \qquad [13]$$

Equation [13] for propylene polymerization is much more facile than Eqn [12] for ethylene because of the greater lability of the β-H and other possible agostic interactions in the former. These reduction/deactivation processes are unfavorable for the zirconocenium systems due to the inaccessibility of the trivalent oxidation state. Therefore, Eqns [12] and [13] are most likely to be the processes responsible for the lower activities for olefin polymerizations by titanocene catalysts than by zirconocene catalysts, and the lower polymerization activities for propylene than ethylene by the same titanocene catalyst.

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