Comparison of Olefin Polymerization Behavior of Catalysts Generated by MAO Activation of Ti^{III} and Ti^{IV} Tris(pyrazolyl)borate Complexes

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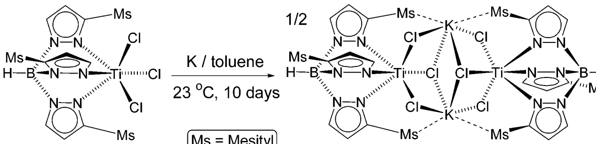
While the identity and reactivity of the $L_nM^{IV}R^+$ active species in Zr and Hf single site olefin polymerization catalysts are reasonably well understood, the chemistry of analogous Ti catalysts is more complex due to the accessibility of both Ti^{III} and Ti^{IV} oxidation states.[1] The active species in catalysts derived from $Cp_2Ti^{IV}X_2$ complexes are $Cp_2Ti^{IV}R^+$ cations, which are rapidly deactivated by reduction to Ti^{III}.[1] Activation of $CpTi^{IV}X_3$ compounds is believed to generate a mixture of Ti^{IV} species, which are active for ethylene and α-olefin polymerization, and Ti^{III} species, which are active for styrene polymerization.[2] In contrast, the bis-allyl complexes $\{(^tBuMe_2SiCH)_2CH\}_2Ti^{III}(\mu\text{-}Cl)_2Li{\cdot}TMEDA$ and $\{(^tBuMe_2SiCH)_2CH\}_2Ti^{IV}Cl_2$ exhibit identical propylene polymerization behavior upon MAO activation, which suggests that the same active species is formed in both cases.[3] Here we report that MAO activation of two closely related tris(pyrazolyl)borate Ti^{III} and Ti^{IV} complexes generates *different* active species and that the distinctive properties of the Ti^{III} system enable the synthesis of polymers that are not accessible with the Ti^{IV} system.

We previously reported that MAO activation of the Ti^{IV} complex $Tp^{Ms}{*}TiCl_3$ (**1**; $Tp^{Ms}{*}$ = HB(3-mesityl-pyrazolyl)$_2$(5-mesityl-pyrazolyl)) generates active ethylene polymerization catalysts.[4] A Ti^{III} analogue of **1**, $K[Tp^{Ms}{*}TiCl_3]$ (**2**), was prepared in 95% yield by reduction of **1** by potassium in toluene (eq 1) and in 22% yield



1; yellow

2; light blue, 95% isol

(1)

by reaction of **1** with KO^tBu.[5] The solid-state structures of **1** and **2** are shown in Figure 1.[6] **2** adopts a dimeric structure in which two $Tp^{Ms}{*}Ti^{III}Cl_3^-$ anions are linked by two K^+ cations, which bind the mesityl and Ti−Cl groups. The Ti−N distances in **2** (average 2.22 Å) are similar to those in **1** (average 2.20 Å). In contrast, the Ti−Cl distances in **2** (average 2.38 Å) are ca. 0.15 Å longer than those in **1** (average 2.23 Å). A similar difference in Ti−Cl distances was observed for $[Me_2HNNMeH][Tp^*Ti^{III}Cl_3]$ (Tp^* = HB(3,5-Me_2-pyrazolyl)$_3$, 2.40 Å)[7] vs $Tp^*Ti^{IV}Cl_3$ (average 2.27 Å).[8] This comparison suggests that the negative charge at Ti rather than the $K^+{\cdots}Cl^-$ ion-pairing lengthens the Ti−Cl bonds in **2**.

Table 1. Ethylene Polymerization Results[a]

entry	catalyst	MAO/M	P^b	MW(10^3)	M_w/M_n
1	Cp_2ZrCl_2	200	5.7	157[c]	3.3
2	Cp_2ZrCl_2[e]	1000	6.5	179[c]	2.8
3	**1**[e]	100	2.8	4810[d]	
4	**1**	200	6.1	930[d]	
5	**1**	1000	3.1	36[c]	14.8
6	**1**	5000	0.8	29[c]	15.5
7	**2**	50	5.5	5215[d]	
8	**2**	100	8.2	2331[d]	
9	**2**	200	7.8	880[d]	
10	**2**	1000	7.2	21[c]	10.2
11	**2**	5000	7.1	11[c]	12.2

[a] Conditions: 80 mL of toluene, 4.2 atm of ethylene, 1 μmol of M (M = Zr or Ti), T_p = 60 °C, time = 6 min. [b] Productivity, average of at least two runs, units: kg/(mmol M atm h). [c] M_p, peak molecular weight determined by GPC using polyethylene calibration. [d] M_v, viscosity-average molecular weight determined by intrinsic viscosity measurement. [e] Reaction stopped at 4 min (entry 2) and 5 min (entry 3).

Ethylene polymerization results for **1**/MAO and **2**/MAO are compared in Table 1 and in the supporting data.[5] Both catalysts exhibit high productivities at low Al loadings (Al/Ti = 200), which are similar to that of Cp_2ZrCl_2/MAO under the same conditions.[9] Both **1** and **2** exhibit increased activity with increasing ethylene pressure[10] and good activity up to 130 °C. Both catalysts produce ultrahigh MW PE (PE = polyethylene) at low Al/Ti ratios, and in both cases MWs drop significantly as the Al/Ti ratio increases. DSC and NMR results establish that the PEs produced by **1**/MAO and **2**/MAO are linear and contain only saturated end groups.[11] These results show that chain transfer to Al is the primary chain transfer mechanism. The PEs from both catalysts have broad MWDs, which may result from changes in $R_{growth}/R_{transfer}$ during the polymerization time due to chain transfer to MAO[4,12] or the heterogeneity of the reaction media resulting from PE precipitation, or from the presence of multiple active species.[13]

However, closer analysis reveals interesting differences between these catalysts. First, productivities based on polymer yields (Table 1) and plots of ethylene consumption rate vs time[5,14] show that **1**/MAO is strongly inhibited at increasing MAO/Ti ratios, but **2**/MAO is not. Second, **1**/MAO exhibits a significant induction period while **2**/MAO does not. Additionally, premixing **1** and MAO prior to exposure to ethylene results in lower activity, indicating that the initially formed species are unstable in the absence of monomer, while the activity of **2**/MAO is unaffected by premixing.[15] Finally, the PE MWs are lower for **2**/MAO than **1**/MAO. Addition of KCl to **1**/MAO does not affect the polymerization behavior. These differences could arise from the presence of different active species, or differences in the activation chemistry, in the two systems. To distinguish these possibilities, ethylene/1-hexene copolymerization studies were performed.

As summarized in Table 2 and Figure 2, **1**/MAO incorporates only minimal hexene to produce toluene-insoluble ethylene/hexene copolymers,[16] while **2**/MAO exhibits excellent hexene incorporation and produces toluene-soluble copolymers. KCl addition does not affect these results. While the copolymers from both catalysts have narrow MWDs characteristic of single site catalysis,[17] TREF and CFC analyses show differences in composition distribution (CD) which reflect differences in the reaction media during copolymerization (**1**/MAO

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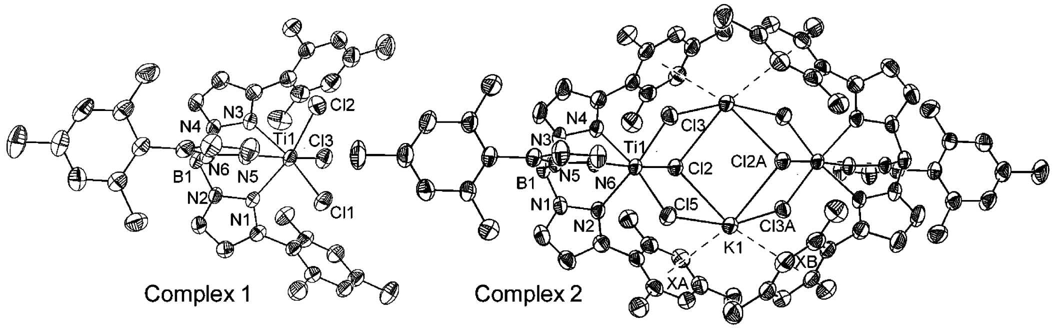

Figure 1. Molecular structures of **1** and **2**.

Table 2. Ethylene/1-Hexene Copolymerization Results[a]

entry	catalyst	MAO/Ti	ethylene (atm)	hexene (M)	P^b	% hexene[c]	r_Er_H	T_m (°C)	MW (10^3)[d]	M_w/M_n
1	**1**	1000	4.2	2	15.7	1.6	8.01	121	51	3.7
2	**1**	1000	4.2	5	18.2	2.7	0.63	116	34	3.5
3	**1**[e]	200	4.2	5	34.9	2.2	2.10	112	440	3.0
4	**2**	1000	4.2	2	50.1	10.1	0.22	115	22	2.3
5	**2**	1000	4.2	5	54.7	16.9	0.41	104	21	2.1
6	**2**	1000	1.4	5	21.6	26.0	0.52	87	12	2.9
7	**2**[f]	200	4.2	5	27.3	13.0	0.81	99	91	2.6

[a] Conditions: toluene/1-hexene total 80 mL, 1 μmol Ti, $T_p = 60$ °C, time = 6 min. [b] Productivity, unit: kg/(mmol Ti h). [c] By ^{13}C NMR. [d] M_p, determined by GPC using polyethylene calibration. [e] Stirring stopped at 2.8 min. [f] Highly viscous mixture.

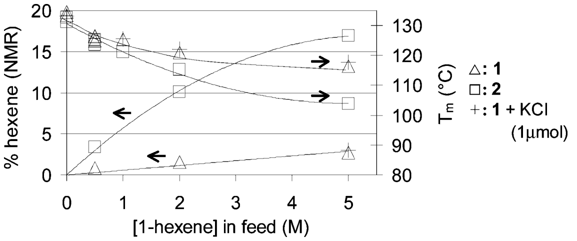

Figure 2. 1-Hexene incorporation by **1** and **2** (Al/Ti = 1000).

slurry; **2**/MAO viscous solution).[18] The copolymers from **2**/MAO have lower MWs than those from **1**/MAO, which suggests that $R_{\text{growth}}/R_{\text{transfer}}$ is decreased following a hexene insertion.[19] These differences in ethylene/hexene copolymerization behavior clearly show that the active species derived from **1**/MAO and **2**/MAO are different.

The copolymers produced by **2**/MAO contain ca. 1−2 methyl branches/chain but no ethyl or propyl branches (^{13}C NMR).[5,11] These observations and the absence of NMR-detectable branches in PE homopolymers producd by **2**/MAO suggest that the methyl branches arise by 1,2-hexene insertion into Ti−CH_3 species at chain initiation and/or by chain transfer to Al following 1,2-hexene insertion rather than by chain-walking. Both **1**/MAO and **2**/MAO produce saturated copolymers consistent with predominant chain transfer to Al as observed in ethylene homopolymerization.

2/MAO can be used to synthesize polymers that are not accessible with **1**/MAO. For example, end-functionalized PEs can be prepared efficiently by ethylene polymerization with **2**/MAO at high [MAO] followed by subsequent reaction of the Al−PE bonds.[20] This is not possible with **1**/MAO because the high [MAO] necessary for efficient chain transfer strongly inhibits activity.

This work shows that MAO activation of Ti^{IV} complex **1** and Ti^{III} complex **2** produces different active species with different olefin polymerization behavior. The data available to date do not allow identification of the structures or oxidation states of the active species in these systems, and given the broad MWDs observed for the PEs, it is possible that multiple active species are formed under some conditions. Further studies may lead to a better understanding of these issues.[21]

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Supporting Information Available: Synthetic details, polymerization results, and X-ray diffraction data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Bond distances (Å) and angles (deg) for **1**: Ti(1)−N(1) = 2.172(3), Ti(1)−N(3) = 2.239(3), Ti(1)−N(5) = 2.183(3), Ti(1)−Cl(1) = 2.22(1), Ti(1)−Cl(2) = 2.26(1), Ti(1)−Cl(3) = 2.20(1), av N−Ti−N 82.2, av Cl−Ti−Cl 96.6; for **2**: Ti(1)−N(2) = 2.221(2), Ti(1)−N(4) = 2.231(2), Ti(1)−N(6) = 2.149(2), Ti(1)−Cl(2) = 2.39(1), Ti(1)−Cl(3) = 2.38(1), Ti(1)−Cl(5) = 2.37(1), K(1)−Cl(2) = 3.05(1), K(1)−Cl(5) = 3.07(1), K(1)−Cl(2A) = 3.06(1), K(1)−Cl(3A) = 3.05(1), K(1)−X(A) = 3.262, K(1)−X(B) = 3.230, av N−Ti−N 84.8, av Cl−Ti−Cl 93.9. X(A) and X(B) are centroids of the mesityl rings.

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(13) M_w/M_n values for entries 3, 4, 7, 8, and 9 are unavailable because the MWs are too high for GPC.

(14) Polymer yields may not reflect true activities as discussed in: Zhou, J.; Lancaster, S. J.; Walker, D. A.; Beck, S.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **2001**, *123*, 223.

(15) A 3 min premix time decreased the productivity of **1**/200 MAO to 1.1 kg/(mmol atm h) (compare to entry 4 of Table 1) but did not affect the productivity of **2**/200 MAO.

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(18) While **1**/1000 MAO yielded narrow CD copolymer, **2**/1000 MAO yielded broad CD copolymer, presumably due to mass transport effects resulting from the viscous reaction mixture. The 1-hexene consumption is $<6\%$ of the initial loading.

(19) **2**/MAO oligomerizes 1-hexene with low activity. (b) The T_m values in Table 2 are influenced by the hexene content and the MW. See: Alamo, R. G.; Chan, E. K. M.; Mandelkern, L. *Macromolecules* **1992**, *25*, 6381.

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