

The formation and polymerization behavior of (pentafluorophenyl)-cyclopentadienyl titanium compounds

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Abstract

$[C_5H_4(C_6F_5)]CpTiCl_3$ (**2**) and $[C_5H_4(C_6F_5)]_2TiCl_2$ (**4**) have been synthesized and are compared with $[C_5H_4(C_6F_5)]_2ZrCl_2$ (**5**), $CpTiCl_3$, Cp_2TiCl_2 and Cp_2ZrCl_2 in their ability to polymerize olefins. The half-sandwich complex **2** is formed by reaction of a trimethylsilyl intermediate with $TiCl_4$. Similarly, the metallocene complex **4** is formed by reaction of a trimethyltin intermediate with $TiCl_4$. EPR measurements of **2**/methylaluminoxane (MAO) and **4**/MAO in toluene solution indicate facile reduction to Ti(III) species occurs. It is suggested that the titanium complexes **2** and **4** with electron-withdrawing pentafluorophenyl substituents favor reduction during polymerizations. This would account for the high activities and stereoregularities observed with **2** for styrene, while poor activities are seen with **4** for ethylene. In general for zirconium compounds, the reduction potential is much lower compared with that of titanium compounds and may be the reason higher activities are observed with **5**. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Polymerizations; Metallocenes; Titanium; Half-sandwich complexes; Electron-withdrawing; Olefins

1. Introduction

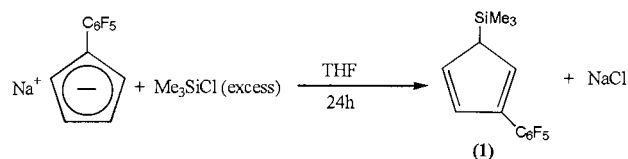
The polymerization behavior of metallocenes on olefins is strongly dependent on the ligand environment. Modification of the steric environment has resulted in higher catalytic activities and improved stereoregularities of the resulting polymer [1]. Recently, research has been geared toward tailoring substituents on a metallocene to determine the effect of changing electron density at the metal center and its overall effect on the polymerization of olefins [2]. In many cases, it was unclear if a steric or an electronic influence of a given substituent was a factor in the polymerization. Recently Deck and Jackson reported the formation of (pentafluorophenyl)-cyclopentadiene and its zirconium derivative $[C_5H_4(C_6F_5)]_2ZrCl_2$ (**5**) [3]. The purpose of this present study was to synthesize the titanocene derivative $[C_5H_4(C_6F_5)]_2TiCl_2$ (**4**) and its half-sandwich complex $[C_5H_4(C_6F_5)]TiCl_3$ (**2**) and to examine their ability to polymerize styrene and ethylene. Compounds **2** and **4** as well as **5** have been compared with their

parent complexes $CpTiCl_3$, Cp_2TiCl_2 and Cp_2ZrCl_2 in order to measure the effect the electron-withdrawing pentafluorophenyl moiety has on the polymerization of olefins.

2. Results and discussion

2.1. Synthesis of catalyst precursors

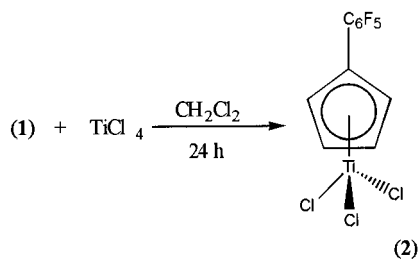
Trimethylsilyl derivatives of cyclopentadiene have been shown to be very effective intermediates in the formation of half-sandwich complexes [4]. (Pentafluorophenyl)-cyclopentadienyl trimethylsilane (**1**) was synthesized in a 66% yield from a reaction of $[C_5H_4(C_6F_5)]^-Na^+$ and chlorotrimethylsilane in THF



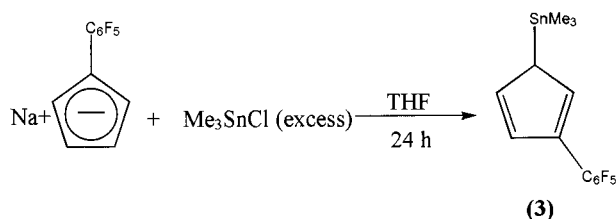
Scheme 1.

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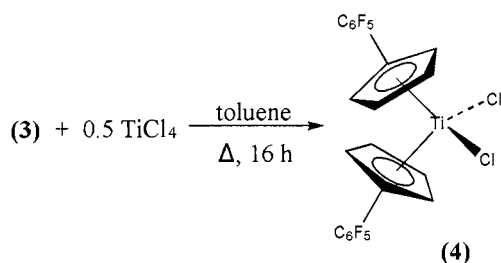
E-mail address: rausch@chem.umass.edu (M.D. Rausch)



Scheme 2.



Scheme 3.



Scheme 4.

for 15 h (Scheme 1). Compound **1** was purified by distillation and was found to be elementally pure. It was then treated with titanium tetrachloride in methylene chloride to give the half-sandwich complex $[\text{C}_5\text{H}_4(\text{C}_6\text{F}_5)]\text{TiCl}_3$ (**2**) in 80% yield (Scheme 2).

Table 1
Polymerization of styrene with **2** and CpTiCl_3 ^a

Catalyst	T_p (°C)	PS (g)	A^b ($\times 10^{-7}$)	T_m^c (°C)	s-PS ^d (%)
2 ^e	20	0.55	1.0	275	95
	20	0.51	0.95		
2 ^e	50	1.62	9.1	277	98
	50	1.59	8.1		
CpTiCl_3 ^f	20	0.33	0.61	262	94
CpTiCl_3 ^f	20	0.35	0.65		
CpTiCl_3 ^f	50	0.76	1.4	264	96
CpTiCl_3 ^f	50	0.75	1.4		

^a Polymerization conditions: MAO used as the co-catalyst; 4000/1 = Al/Ti; 50 μM catalyst solution in toluene; 5 ml of styrene as monomer.

^b A (activity) = g PS/[mol Ti] [Styrene](h).

^c T_m , melting temperature of polymer.

^d % s-PS = [g of 2-butanone insoluble polymer]/(g of bulk polymer) $\times 100$.

^e 10 min polymerization.

^f 30 min polymerization.

We found that the titanocene $[\text{C}_5\text{H}_4(\text{C}_6\text{F}_5)]_2\text{TiCl}_2$ (**4**) could be synthesized in good yield from the reaction of the trimethyltin intermediate **3** with TiCl_4 . Compound **3** was prepared from the reaction of $[\text{C}_5\text{H}_4(\text{C}_6\text{F}_5)]^- \text{Na}^+$ with trimethyltin chloride in THF for 24 h (Scheme 3). Compound **3** was obtained in 31% yield as a clear oil by distillation. Treatment of **3** with titanium tetrachloride in refluxing toluene for 16 h subsequently afforded **4** in 51% yield after recrystallization from hot toluene (Scheme 4).

Compound **4** is a dichroic complex that changes from a dark-green to a violet color on exposure to light. This compound was also characterized by $^1\text{H-NMR}$ and elemental analysis and was found to be elementally pure. Initially, we tried to form **4** via the trimethylsilyl route as described above using an excess of **1**. However, even refluxing the reaction for 24 h in toluene only led to the formation of the half-sandwich complex $[\text{C}_5\text{H}_4(\text{C}_6\text{F}_5)]\text{TiCl}_3$ (**2**). It is clear that the trimethyltin route is more effective in generating metallocenes of this type.

2.2. Polymerization results

Group IV half-sandwich catalysts are known to give high activity for styrene when activated by methylaluminoxane [5]. Compound **2** was examined as a styrene polymerization catalyst and was compared with the parent compound CpTiCl_3 (Table 1).

It can be seen that compound **2** shows a significantly higher activity, percentage syndiotacticity and T_m than CpTiCl_3 . The activity is a factor of ten higher at 50°C and the T_m is more than ten degrees higher at both temperatures. The current mechanism for styrene polymerization indicates that a multihapto coordination occurs between the cationic center, the styrene monomer and the propagating chain [6a]. Studies have proposed that a Ti(III) oxidation state is active for

Table 2
Polymerization of ethylene with **5**, **4**, Cp₂TiCl₂ and Cp₂ZrCl₂^a

Catalyst	T _p (°C)	PE (g)	A ^b (× 10 ⁻⁶)	T _m ^c (°C)
5 ^d	20	2.15	3.0	133.2
5 ^d	20	2.04	2.9	
5 ^e	50	4.05	31	135.1
5 ^e	50	4.08	32	
Cp ₂ ZrCl ₂ ^f	20	6.42	42	138.3
Cp ₂ ZrCl ₂ ^f	20	6.18	40	
Cp ₂ ZrCl ₂ ^f	50	5.92	38	137.2
Cp ₂ ZrCl ₂ ^f	50	5.61	33	
4 ^g	20	0.388	0.42	115.9
4 ^g	20	0.372	0.40	
4 ^g	50	0.091	0.14	119.0
4 ^g	50	0.11	0.16	
Cp ₂ TiCl ₂ ^h	20	0.85	11.1	135.8
Cp ₂ TiCl ₂ ^h	20	0.77	9.9	
Cp ₂ TiCl ₂ ^h	50	0.74	13	134.5
Cp ₂ TiCl ₂ ^h	50	0.75	13	

^a Polymerization conditions: MAO used as co-catalyst, 4000/1: Al/Ti or Al/Zr; 1 ml of catalyst solution inject into polymerization bottle.

^b A (activity) = g PE/[(mol Ti) [ethylene] (h)].

^c T_m, melting temperature of polymer.

^d 38 μM catalyst solution in toluene, 1 h polymerization.

^e 38 μM catalyst solution in toluene, 15 min polymerization.

^f 50 μM catalyst solution in toluene, 10 min polymerization.

^g 50 μM catalyst solution in toluene, 1 h polymerization.

^h 50 μM catalyst solution in toluene, 5 min polymerization.

Table 3
Polymerization of ethylene with **5**, **4**, Cp₂TiCl₂, and Cp₂ZrCl₂^a

Catalyst	PE (g)	A ^b (× 10 ⁻⁶)	T _m ^c (°C)
5 ^d	0.97	3.7	124
5 ^d	0.91	3.6	
Cp ₂ ZrCl ₂ ^d	0.96	3.7	124
Cp ₂ ZrCl ₂ ^d	0.99	3.8	
4 ^e	0.28	0.52	121
4 ^e	0.31	0.53	
Cp ₂ TiCl ₂ ^d	1.7	6.3	130
Cp ₂ TiCl ₂ ^d	1.6	6.0	

^a Polymerization conditions: polymerization performed at 0°C; 20/1: TIBA/Ti or TIBA/Zr; 1:1 trityl/catalyst; 50 μM catalyst solution in toluene; 1 ml of catalyst solution injected in polymerization bottle.

^b A (activity) = g PE/[(mol Ti) [ethylene](h)].

^c T_m, melting temperature of polymer.

^d 15 min polymerization.

^e 1 h polymerization.

styrene polymerization [6] due to this mechanism. It has been shown that a typical co-catalyst causes reduction of metallocenes and half-sandwich complexes during polymerizations [6c,7]. EPR spectroscopy was performed using **2**/methylaluminumoxane (MAO) and **4**/MAO in toluene solutions. Both solutions rapidly changed to a light-green color on exposure to MAO. An EPR spectrum recorded after 5 min show a well-defined doublet at $g = 2.0045$ with a splitting of 7.4 G for **2**/MAO. In addition, **4**/MAO showed a similar

splitting pattern with $g = 1.988$ with a splitting of 7.2 G. Both EPR spectra are consistent with the proposed Ti(III) reductive species. Additional satellites are also seen in the spectra but are less pronounced.

Preactivation was also attempted with **2** as a catalyst under the same conditions as above. However, there was only a slight increase in activity observed. This result suggests that there is a very short induction time to form the alkylated species, the resulting cation after methide abstraction, and reduction of the catalyst species to Ti(III) by MAO. This is probably due to the electron-withdrawing pentafluorophenyl groups increasing the electrophilicity and reactivity of the catalyst.

Ethylene polymerizations were carried out using **4** and [C₅H₄(C₆F₅)₂ZrCl₂ (**5**). These complexes were compared to Cp₂ZrCl₂ and Cp₂TiCl₂ (Table 2).

Low-temperature polymerizations of ethylene with **5**, **4**, Cp₂TiCl₂, and Cp₂ZrCl₂ were also carried using trityl tetrakis(pentafluorophenyl borate, [CPh₃]⁺ B[C₆F₅]₄⁻ (TIBA) [8] as the co-catalyst. The polymerization results are given in Table 3.

As seen in Tables 2 and 3, **4** shows much lower activity and T_m than Cp₂TiCl₂. Studies have shown that reduction of the catalytic species can occur during polymerizations and it is believed that ethylene is polymerized with low productivity when the catalyst is in the Ti(III) oxidation state [6c,7]. Titanium complexes have a high reduction potential and are easily reduced to the Ti(III) state. We have confirmed via EPR measurements that both **2** and **4** are readily reduced to a Ti(III) species by excess MAO in toluene solutions. We believe this electronic effect is observed in our catalyst system because reduction in the presence of MAO or trityl/TIBA is more favorable with a highly electrophilic center. With compound **4**, the rate of reduction of the catalyst species should increase as the temperature increases and this may explain why lower activities are observed at higher temperatures. Zirconium compounds are more difficult to reduce to the Zr(III) state and this may explain why there is no dramatic difference in the activities of **5** and Cp₂ZrCl₂ compared to **2** and Cp₂TiCl₂.

Recently, Rausch and co-workers performed polymerizations of ethylene with titanocene dichloride, and its bis(trifluoromethyl) and bis(*N,N*-dimethylamino) derivatives with MAO and trityl/TIBA co-catalysts [2e]. In these systems, they found that the electron-withdrawing bis(trifluoromethyl) derivative [C₅H₄(CF₃)₂-TiCl₂ gave lower activities at both low and elevated temperatures compared with the parent compound Cp₂TiCl₂. It was concluded that reduction of the catalytic species could have occurred, resulting in lower activities.

We have shown that **2** is an excellent catalyst precursor for the polymerization of styrene while **4** is a relatively poor catalyst for ethylene. EPR studies

confirm that the highly electrophilic titanium complexes **2** and **4** in toluene solutions undergo facile reduction to the Ti(III) species in the presence of MAO. Reduction is not favorable in **5** due to its much lower reduction potential than that of titanium.

3. Experimental

Reactions were carried out under an argon atmosphere using standard Schlenk techniques. MAO was purchased from Akzo Nobel. THF, pentane, hexane and toluene were distilled from Na/K alloy under argon. Methylene chloride was distilled from CaH₂. Styrene was distilled from CaH₂ in vacuo prior to use. Dicyclopentadiene was cracked prior to use. [C₅H₄(C₆F₅)₂ZrCl₂ (**5**) and [C₅H₄(C₆F₅)]⁻Na⁺ were prepared by literature procedures [3]. Trityltetrakis(pentafluorophenyl)borate, [CPh₃]⁺B[C₆F₅]₄⁻, was synthesized by literature procedure [8]. All other chemicals were purchased from Aldrich and used without further purification. ¹H-NMR spectra were recorded on a Bruker-200 spectrometer. EPR measurements were performed on a Bruker-300 MHz spectrometer. Elemental analyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

3.1. Synthesis of (pentafluorophenyl-cyclopentadienyl)trimethylsilane (**1**)

To a solution of [C₅H₄(C₆F₅)]⁻Na⁺ (5.1 g, 20 mmol) in 100 ml of THF, chlorotrimethylsilane (slight excess) (3.1 ml, 23 mmol) was added and the solution changed from a deep-violet to a light-orange color. The resulting solution was allowed to stir overnight. The solvent was removed and the resulting oil was extracted with 100 ml of hexane. After removal of the hexane, the resulting oil was distilled at 70°C/0.01 mmHg to give 4.01 g of **1** as a mixture of isomers in 66% yield. ¹H-NMR (CDCl₃): δ 6.62–7.3 (m, 3H), 3.21–3.8 (m, 1H), –0.0162–0.21 (m, 9H). Anal. Calc. for C₁₄H₁₃F₅Si: C, 55.25; H, 4.30. Found: C, 55.08; H, 4.17%.

3.2. Synthesis of [C₅H₄(C₆F₅)]TiCl₃ (**2**)

To a solution of (pentafluorophenyl-cyclopentadienyl)trimethylsilane (**1**) (2.00 g, 6.6 mmol) in 50 ml of CH₂Cl₂, TiCl₄ (0.71 ml, 6.6 mmol) was added at 0°C. The mixture was warmed to room temperature (r.t.) and allowed to stir overnight. The solvent was removed and the resulting orange solid was sublimed at 70°C/0.01 mmHg to give 2.02 g of pure **2** as orange crystals in 80% yield. ¹H-NMR (CDCl₃): δ 7.46 (m, 2H), 7.17 (t, 2H). Anal. Calc. for C₁₁H₄Cl₃F₅Ti: C, 34.28; H, 1.05. Found: C, 34.21; H, 1.07%.

3.3. Synthesis of (pentafluorophenyl-cyclopentadienyl)trimethyltin (**3**)

To a solution of [C₅H₄(C₆F₅)]⁻Na⁺ (5.1 g, 20 mmol) in 100 ml THF, trimethyltin chloride (4.3 g 22 mmol) was added as a solid and the solution changed from a deep-violet to an orange color. The resulting solution was allowed to stir overnight. The solvent was removed and the resulting red oil was extracted with 100 ml of hexane. After removal of the hexane the red oil was distilled at 100°C/0.01 mmHg to give 2.68 g of pure **3** in 31% yield as a mixture of isomers. ¹H-NMR (CDCl₃): δ 5.72–7.21 (m, 3H), 3.12–3.45 (m, 1H), –0.021–0.5 (m, 9H).

3.4. Synthesis of [C₅H₄(C₆F₅)₂TiCl₂ (**4**)

To a solution of TiCl₄ (0.27 ml, 2.5 mmol) in 50 ml of toluene, (pentafluorophenyl-cyclopentadienyl)trimethyltin (**3**) (2.0 g, 5.0 mmol) (dissolved in 5 ml of hexane) was added at 0°C and the resulting solution was warmed to r.t. and refluxed overnight. The resulting red solution was cooled and the solvent was removed in vacuo. The resulting red oil was triturated and washed with several portions of hexane. Toluene (20 ml) was added and the suspension was then heated and quickly filtered via cannula while hot to give 0.72 g of pure **4** in 51% yield after cooling and removal of the solvent. ¹H-NMR (CDCl₃): δ 7.15 (m, 4H), 6.67 (t, 4H). Anal. Calc. for C₂₂H₈Cl₂F₁₀Ti: C, 45.47; H, 1.39. Found: C, 45.64; H, 1.63%.

3.5. Polymerizations

Polymerizations were carried out in 250 ml crown-capped glass pressure reactors containing 50 ml of freshly distilled toluene and the desired monomer. For ethylene polymerizations, the system was saturated with ethylene at 15 psig. Styrene polymerizations were carried out using 5 ml of freshly distilled styrene from CaH₂. The system was then injected with the desired amount of MAO and was left to stir for 10 min. The polymerizations were initiated by adding the desired catalyst in a solution of toluene to the reactors. The catalyst was preactivated by injecting 1 ml of MAO to the catalyst solution and this was left to stir for 15 min. Trityl/TIBA polymerization were performed by adding a 20-fold excess of TIBA to the toluene solution of monomer, followed by the desired amount of catalyst and finally [CPh₃]⁺B[C₆F₅]₄⁻. The polymerizations were terminated by adding 2% HCl–methanol solution. The polymers were then filtered, dried and weighed. The bulk polymer in the case of polystyrene was obtained by using a Soxhlet extractor for 24 h in 2-butanone to determine the percentage s-PS. The melting points of the polymers were obtained by DSC.

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