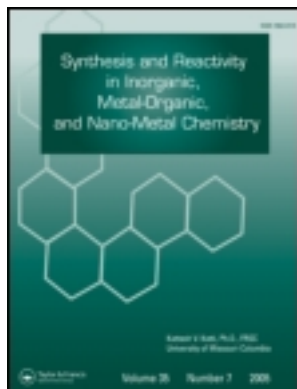


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## Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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### Synthesis and Characterization of Cyclopentadienyl Titanium Trichloride and Indenyltitanium Trichloride; Monocyclictitanium Trihalide Complexes

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# Synthesis and Characterization of Cyclopentadienyl Titanium Trichloride and Indenyltitanium Trichloride; Monocyclictitanium Trihalide Complexes

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**CpTiCl<sub>3</sub> and IndTiCl<sub>3</sub> are homogeneous metallocene catalysts that are produced under highly controlled conditions. Syndiotactic polymerization of styrene is carried out using these catalysts while methylaluminoxane (MAO) is used as a cocatalyst. In the present paper synthesis of CpTiCl<sub>3</sub> was examined at first by reacting TiCl<sub>4</sub> with CpNa, this reaction just led to formation of Cp<sub>2</sub>TiCl<sub>2</sub> so CpNa was not a suitable Cp donor compound, therefore CpSiMe<sub>3</sub> was used instead of CpNa. Reaction of CpSiMe<sub>3</sub> with TiCl<sub>4</sub>, produced CpTiCl<sub>3</sub> immediately. IndTiCl<sub>3</sub> was synthesized by reacting IndSiMe<sub>3</sub> and TiCl<sub>4</sub> as well. At the end two synthetic catalysts were characterized by FTIR and <sup>1</sup>H-NMR spectrometers.**

**Keywords** monocyclic, synthesis, sodium cyclopentadienide, trimethylsilylcyclopentadiene, cyclopentadienyltitanium trichloride, indenyltitanium trichloride

## INTRODUCTION

Since the discovery of the Ziegler–Natta catalyst systems in the early 1950s, the metallocene complexes of group IVB metals have become an important class of homogeneous catalysts for the polymerization of  $\alpha$ -olefins. Metallocene catalysts have become increasingly important as part of potentially new generation of Ziegler–Natta (ZN) catalyst. As an advantage over the conventional ZN catalyst, metallocene or single site catalyst have the capability of better control of polymer tacticity, molecular weight, and molecular weight distribution.<sup>[1–4]</sup>

The use of TiCl<sub>4</sub>-methylalumoxane (MAO) system in the first preparation of syndiotactic polystyrene by Ishihara has led scientists to observe that titanium compounds of the type Cp'TiX<sub>3</sub> (Cp' = C<sub>5</sub>H<sub>5</sub>, C<sub>5</sub>Me<sub>5</sub>, C<sub>5</sub>Me<sub>4</sub>H or C<sub>9</sub>H<sub>7</sub>; X = halide, alkoxides or alkyl groups) are among the most effective catalysts for preparation of syndiotactic polystyrene (sPS).<sup>[5,6]</sup>

In 1986 Ishihara found that cyclopentadienyltitanium trichloride (CpTiCl<sub>3</sub>) as half-sandwich catalyst produce sPS.<sup>[7–9]</sup> It is worth noting that biscyclopentadienyltitanium dichloride does not promote syndiospecific polymerization of styrene.<sup>[10]</sup> In 1993, Rausch and coworkers reported the first sPS catalyst containing indenyl and found that the ( $\eta^5$ -indenyl)TiCl<sub>3</sub>–MAO system catalyzed the polymerization of styrene over a wide range of polymerization temperature more effectively than CpTiCl<sub>3</sub>–MAO.<sup>[11]</sup>

Indenyltrichloro titanium activated with MAO is a catalyst exceedingly high in both activity and specificity<sup>[9,11]</sup> and which is relatively insensitive to polymerization conditions.<sup>[11,12]</sup>

Greater activity for IndTiCl<sub>3</sub> may be attributed to the higher propagation rate due to the greater electron-donating ability of the indenyl group ring relative to the Cp moiety.<sup>[11]</sup> This paper reports two different synthesis methods of simple single-ring cyclopentadienyltitanium trichloride and a method for synthesis of indenyltitanium trichloride.

## EXPERIMENTAL

CpTiCl<sub>3</sub> and IndTiCl<sub>3</sub> catalysts were prepared according to methods obtained from literature and developed in Polymer and Petrochemical Institute of Iran (IPPI).<sup>[9]</sup> All operations were performed under pure N<sub>2</sub> atmosphere using a dry box equipped with gas driers such as KOH, silica gel and molecular sieve 4 Å.

## Materials

Commercially available titanium tetrachloride (Merck), trimethylsilylindene (Aldrich), 2 M solution of sodium cyclopentadienide in THF (Aldrich) and dichloromethane (Aldrich) were used without further purification. n-Hexane (Iran Petroleum Co.) was distilled over calcium hydride. Toluene, tetrahydrofuran and benzene (Merck) were refluxed over metallic sodium and benzophenone as an indicator. Reactants were introduced to the degassed flasks under nitrogen (99.999%).

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Anhydrous  $\text{MgSO}_4$  (Scharloo) was used to dry a compound during the synthesis. Two different methods to synthesis of  $\text{CpTiCl}_3$  were used.

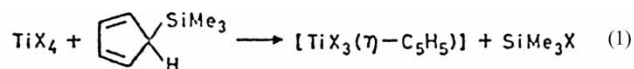
### SYNTHESIS OF CYCLOPENTADIENYL TITANIUM TRICHLORIDE

#### Synthesis of $\text{CpTiCl}_3$ with $\text{CpNa}$

Sixty-one mL of 2 M solution of sodium cyclopentadienide in tetrahydrofuran containing 0.12 mol  $\text{CpNa}$  was added drop wise at  $0^\circ\text{C}$  to 0.12 mol of  $\text{TiCl}_4$  that was dissolved in 200 mL of toluene. The reaction mixture was allowed to stand overnight at room temperature then it was filtered. The filtrate was stored at refrigerator for a few days and some red crystals appeared in the solution.<sup>[13]</sup> The compound (**1a**) was characterized by its  $^1\text{H-NMR}$  and FTIR spectra.

#### Synthesis of $\text{CpTiCl}_3$ with $\text{CpSiMe}_3$

Trimethylsilylcyclopentadiene was prepared by treating sodium cyclopentadienide (1 mol) with chlorotrimethylsilane (1 mol). Then  $\text{CpSiMe}_3$  was reacted with  $\text{TiCl}_4$  to form  $\text{CpTiCl}_3$  as Equation (1).<sup>[14]</sup>



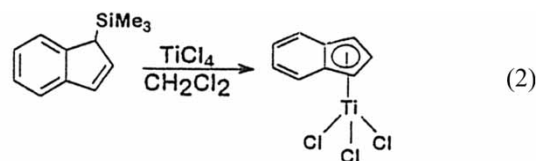
#### Preparation of Trimethylsilylcyclopentadiene

To a solution of 0.2 mol of sodium cyclopentadiene in 100 mL of dry THF was added drop wise 0.2 mol of chlorotrimethylsilane in 50 mL of dry THF at  $0^\circ\text{C}$  with stirring under  $\text{N}_2$  atmosphere. After the addition was completed the resulting reaction mixture was stirred for 1 h at room temperature. The reaction mixture was poured into a large amount of water; the organic phase was separated and dried over  $\text{MgSO}_4$ , and then concentrated to leave a residue. The residue was distilled under reduced pressure to give trimethylsilylcyclopentadiene as an isomeric mixture: colorless liquid; bp.  $50\text{--}55^\circ\text{C}/10\text{ mmHg}$ .<sup>[8,14–16]</sup> The compound was characterized by its  $^1\text{H-NMR}$  spectrum.

#### Reaction of Trimethylsilylcyclopentadiene with Titanium Tetrachloride

To 66 mmol titanium tetrachloride in 40 mL of benzene was slowly added 66 mmol of trimethylsilylcyclopentadiene with stirring. The reaction was rather violent with evolution of heat and precipitation of a yellow solid was virtually immediate. The reaction mixture was stirred for a further 30 minute. The product was filtered off. Washed with two 20 mL portion of benzene and dried under vacuum.<sup>[14,16]</sup> The compound (**1b**) was characterized by its  $^1\text{H-NMR}$  and FTIR spectra. Anal. Calcd. for  $\text{CpTiCl}_3$ (%): C, 27.37; H, 2.30<sup>[17]</sup>. Found: C, 27.68; H, 2.11.

### SYNTHESIS OF INDENYL TITANIUM TRICHLORIDE



First, 26.4 mmol of  $\text{TiCl}_4$  was dissolved in 70 mL of dichloromethane in a 250 mL flask, equipped with magnetic stirrer and an addition funnel. Then 31.2 mmol of trimethylsilylindene that was dissolved in 30 mL of dichloromethane, was added drop wise, while the temperature was maintained at  $0^\circ\text{C}$ . The initially yellow solution slowly turned deep-red. The mixture stirred overnight at room temperature before the solvent was removed under vacuum. To the dark-red residue, 100 mL of hexane was added and the resultant suspension was cooled to  $-30^\circ\text{C}$  for several hours. A dark-violet precipitate formed which was collected by filtration, washed with cold hexane, and dried under vacuum. The compound was characterized by its  $^1\text{H-NMR}$  spectrum.

### CHARACTERIZATION

The synthetic catalysts were characterized by BRUKER, IFS48 infrared spectrometer and the BRUKER 400 MHz AVANCE 400 nuclear magnetic resonance spectrometer and Elementar Analysensysteme GmbH VarioEL.

### RESULT AND DISCUSSION

#### Infrared Spectra

The infrared absorption spectra of **1a** and **1b** (Figures 1 and 2) were compared with reference spectra and it was found that **1a** was  $\text{Cp}_2\text{TiCl}_2$  and **1b** was  $\text{CpTiCl}_3$ . The characteristic peaks are  $833, 935, 1017, 1433, 3107\text{ cm}^{-1}$  for  $\text{CpTiCl}_3$ <sup>[18]</sup> and  $820, 866, 1016, 1439, 3099\text{ cm}^{-1}$  for  $\text{Cp}_2\text{TiCl}_2$ .<sup>[19]</sup>

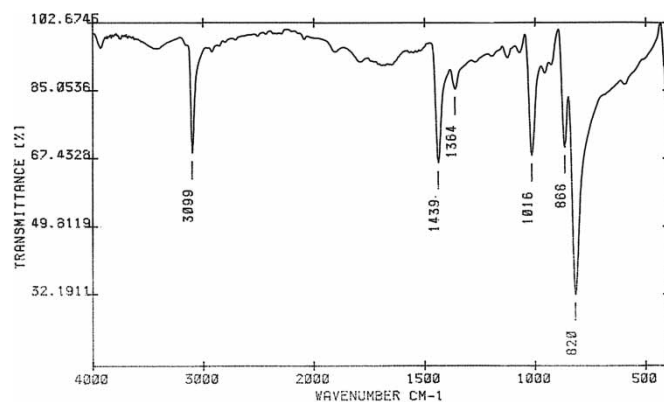


FIG. 1. FTIR spectrum of **1a**, the product of the reaction of  $\text{CpNa}$  with  $\text{TiCl}_4$ .

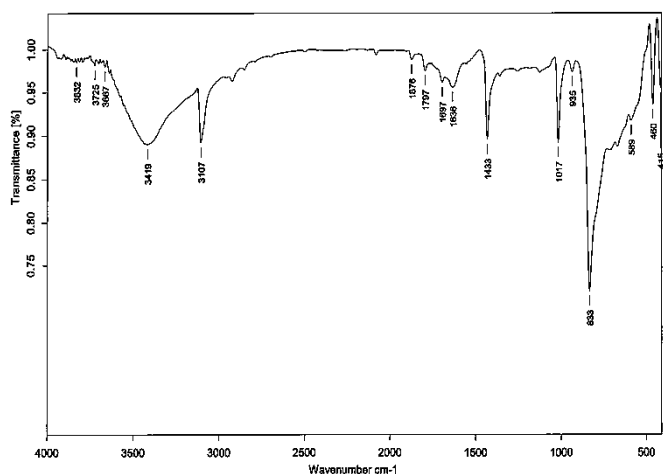


FIG. 2. FTIR spectrum of **1b**, the product of the reaction of  $\text{CpSiMe}_3$  with  $\text{TiCl}_4$ .

Moffitt<sup>[20]</sup> characterized the cyclopentadienyl radical in bis-cyclopentadienyl titanium dibromide as a five membered aromatic ring bonded to the central metal atom through the  $\pi$  orbitals. The evidences suggest that such a structure exists also in  $\text{Cp}_2\text{TiCl}_2$  and  $\text{CpTiCl}_3$ . For both  $\text{CpTiCl}_3$  and  $\text{Cp}_2\text{TiCl}_2$  the presence of a single band in the C-H stretch ( $3107$  and  $3099\text{ cm}^{-1}$ ) and C-H bend regions ( $1433$  and  $1439\text{ cm}^{-1}$ ) and the absence of peaks in the C=C stretch region ( $1575\text{--}1700\text{ cm}^{-1}$ ) suggest for the ring a resonance structure in which there are no formal double bonds. The strong infrared band at  $770\text{ cm}^{-1}$  postulated by Sloan and Barber<sup>[20]</sup> to be characteristic of mono-ring titanium trihalides is absent so it is in agreement with the results obtained by Reid and Wailes.<sup>[18]</sup>

### Proton Magnetic Resonance Spectra

The  $^1\text{H-NMR}$  spectrum obtained for solution of  $\text{Cp}_2\text{TiCl}_2$  in DMSO (Figure 3) shows one very sharp peak at  $6.6\text{ ppm}$ .<sup>[18]</sup> This data is consistent with a structure in which all the protons are equivalent. It can be concluded that in this compound two  $\text{C}_5\text{H}_5$  rings are similarly  $\pi$ -bonded. A  $\pi$ -bonded structure results in five equivalent hydrogen atom positions.<sup>[21]</sup>

In the  $^1\text{H-NMR}$  spectrum of  $\text{CpSiMe}_3$  in benzene (Figure 4), there are two doublets at  $6.6$  and  $6.8\text{ ppm}$  that are related to the four vinylic protons of the Cp ring and there is a single peak at  $3.3\text{ ppm}$ , which is related to the nonvinylic  $\text{sp}^3$  proton of the Cp ring. It has been reported that 1-trimethylsilylcyclopentadiene converts to 2-trimethylsilylcyclopentadiene and then to 3-trimethylsilylcyclopentadiene with increasing temperature and also with the time of storage as Scheme 1.<sup>[22–25]</sup>

Because of weaker intensity of the peak that is at the lower magnetic field of the spectrum, it can be concluded that some portion of the 1-trimethylsilylcyclopentadiene has been converted to the 2-trimethylsilylcyclopentadiene because of

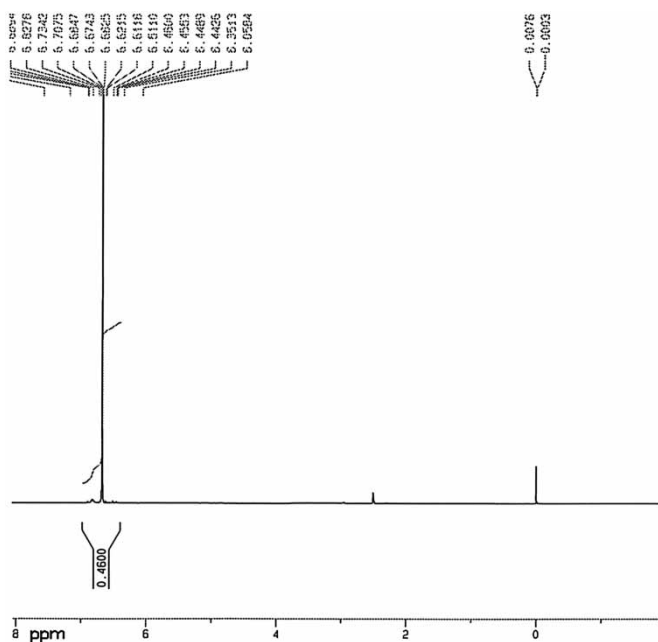


FIG. 3.  $^1\text{H-NMR}$  spectrum of  $\text{Cp}_2\text{TiCl}_2$  in DMSO.

being at room temperature for about half an hour before taking  $^1\text{H-NMR}$  spectrum.

Two singlet peaks of  $^1\text{H-NMR}$  spectrum of  $\text{CpTiCl}_3$  in  $\text{CHCl}_3$  (Figure 5), at  $6.9$  and  $7.03\text{ ppm}$  indicate that unlike  $\text{Cp}_2\text{TiCl}_2$  that has a single peak in  $^1\text{H-NMR}$  spectrum;  $\text{C}_5\text{H}_5$  ring does not settle symmetrically on the Ti element in  $\text{CpTiCl}_3$ , so two separate sharp peaks appeared.<sup>[26]</sup>

In the  $^1\text{H-NMR}$  spectrum of  $\text{IndTiCl}_3$  in benzene (Figure 6), it can be seen that there are four groups of hydrogen with the

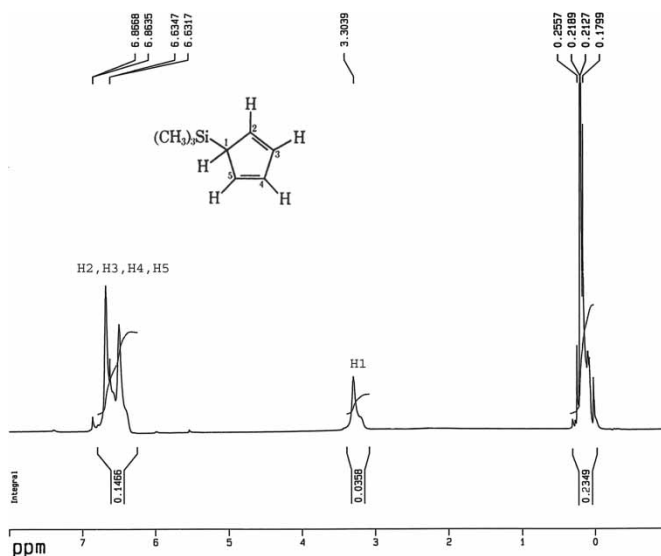
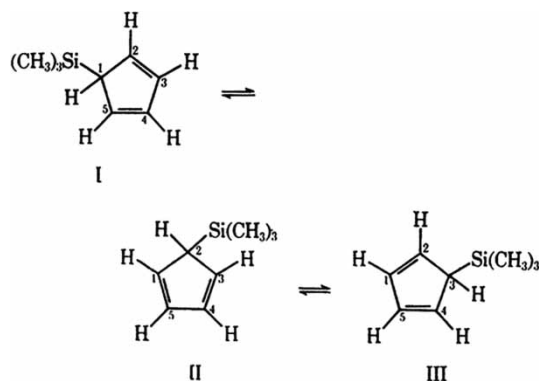


FIG. 4.  $^1\text{H-NMR}$  spectrum of  $\text{CpSiMe}_3$  in benzene.



SCH. 1. Temperature and time dependent equilibrium among trimethylsilyl-cyclopentadiene isomers.

chemical shifts at 6.26 t 1H, 6.38 d 2H, 6.85 did 2H and 7.15 m 2H related to cyclic protons.<sup>[27]</sup>

## CONCLUSION

It was found that the  $\text{CpTiCl}_3$  can be obtained in a high yield in a single step reaction, syndiotactic polymerization of styrene was carried out with this catalyst and optimum conditions was obtained for polymerization and polymers were characterized.<sup>[28]</sup>

- Attempt to isolate  $\text{CpTiCl}_3$  from the reaction of  $\text{TiCl}_4$  with  $\text{CpNa}$  was unsuccessful.
- The synthesis of  $\text{CpTiCl}_3$  by reaction of  $\text{TiCl}_4$  and  $\text{CpSiMe}_3$  as a Cp donor compound instead of  $\text{CpNa}$ , lead to the formation of  $\text{CpTiCl}_3$  immediately.
- The advantage of  $\text{CpSiMe}_3$  is that, firstly it doesn't replace two Cp rings in the  $\text{TiCl}_4$  even by unlimited

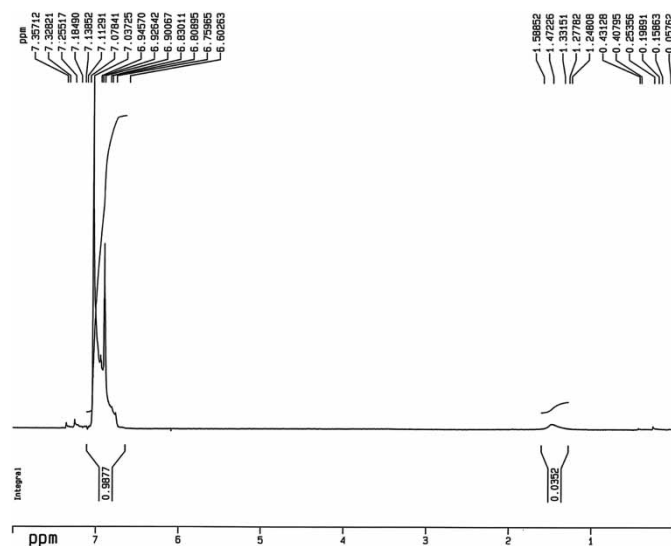


FIG. 5.  $^1\text{H-NMR}$  spectrum of  $\text{CpTiCl}_3$  in  $\text{CHCl}_3$ .

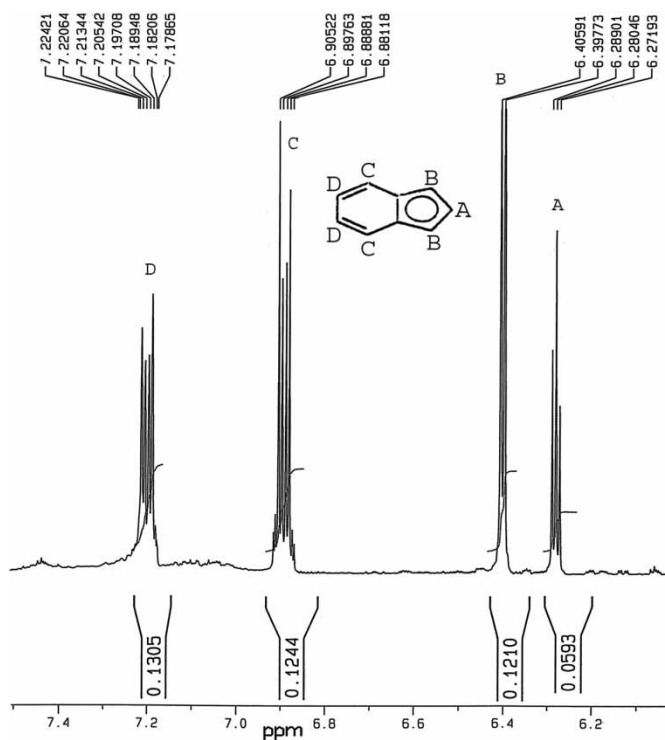


FIG. 6.  $^1\text{H-NMR}$  spectrum of  $\text{IndTiCl}_3$  in benzene.

reaction time; secondly the product is easily separated by filtration.

- The disadvantage of  $\text{CpSiMe}_3$  is that it is time and temperature dependent and converts to vinylic isomers. So it should be consumed just after distillation to prevent formation of undesirable isomers.
- As well the use of  $\text{IndSiMe}_3$  as an indenyl group donor in the synthesis of  $\text{IndTiCl}_3$  by reacting  $\text{TiCl}_4$  with  $\text{IndSiMe}_3$  was successful.

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