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The synthesis and polymerization behavior of methoxy-substituted (indenyl) trichlorotitanium complexes

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Abstract

A variety of methoxy-substituted (indenyl)trichlorotitanium complexes were synthesized, and these precursors were used to polymerize styrene, ethylene, and propylene. The complexes, when activated with methylaluminoxane (MAO), show only low activity for α-olefin polymerization. Oxygen–aluminum coordination between the methoxy group and MAO could be the deactivating interaction.

1. Introduction

In 1986 Ishihara and coworkers reported that $CpTiCl_3$ with methylaluminoxane (MAO) as a cocatalyst produced syndiotactic polystyrene (s-PS) for the first time [1]. Since the initial discovery, several studies on the effect of ligand substitution on polymerization behavior [2,3], as well as studies on the mechanism involved in the polymerization of styrene, have been reported [4].

We have recently reported that {[2-(dimethylamino)ethyl]cyclopentadienyl}trichlorotitanium (1) is a catalyst for styrene polymerization when activated with MAO. In addition, 1–MAO was also found to be active for the polymerization of ethylene and propylene [5]. The ability of this catalyst to polymerize all three monomers can be attributed to the fact that the dimethylamino group is able to coordinate reversibly to the titanium center in the activated species.

It has been shown by Yanlong and coworkers [6] that in the precursor [(2-methoxyethyl)cyclopentadienyl]tri-

chlorotitanium (2) there is chelation of the oxygen atom to the titanium center prior to activation by MAO.

1   2

The central purpose of the present study is to investigate the influence of methoxy substituents on polymerization behavior. Several methoxy-substituted catalyst precursors were synthesized and evaluated as catalyst precursors to polymerize α-olefins.

2. Experimental section

Reactions were carried out under an argon atmosphere using standard Schlenk techniques. MAO was purchased from Akzo, and all other reagents were purchased from Aldrich and used without further purification. 4,7-Dimethoxyindene [7], 3-methoxyindene [8],

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(2-methoxyethyl)cyclopentadiene [9], and 3-(2-methoxyphenyl)indene [10] were prepared by literature procedures. Toluene, diethyl ether, tetrahydrofuran (THF), hexane and pentane were distilled from Na–K alloy under argon. Methylene chloride and styrene were distilled under argon from CaH_2. ^1H NMR spectra were recorded on Varian XL-200 or Bruker NR-80 spectrometers. Elemental analyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA. The procedure used to polymerize styrene has been reported in detail [3].

2.1. 4,7-Dimethoxy-1-trimethylsilylindene (3)

To a solution of 4,7-dimethoxyindene (1.6 g, 9.0 mmol) in 50 ml of THF was added a 1.6 M solution of butyllithium in hexane (5.6 ml, 9.0 mmol) at 0 °C and the solution was stirred for 8 h at room temperature. The solvent was removed under reduced pressure, and the residue was dissolved in 75 ml of hexane. Chlorotrimethylsilane (1.20 g, 11 mmol) was added at 0 °C, and the mixture was stirred overnight at room temperature. The suspension was filtered and the solvent removed under reduced pressure to give 1.6 g (72%) of 3 as a yellow oil. ^1H NMR (CDCl$_3$): δ 7.08–6.54 (2H, m, H$_{2,3}$); 6.65 (2H, s, H$_{5,6}$); 3.88 (3H, s, OCH$_3$); 3.83 (3H, s, OCH$_3$); 3.71 (1H, s, H$_1$); −0.01 (9H, s, SiMe$_3$).

2.2. (η^5-4,7-Dimethoxyindenyl)trichlorotitanium (4)

A solution of 3 (1.6 g, 6.4 mmol) in 50 ml of CH$_2$Cl$_2$ was cooled to 0 °C and TiCl$_4$ (1.5 g, 7.7 mmol) was slowly added via a syringe. The reaction mixture was stirred at 0 °C for 30 min and at room temperature for 8 h. The solvent was removed under reduced pressure, and the solid residue was washed with hexane and dried in vacuo. The solid was vacuum sublimed at 140 °C/0.003 mm Hg to give 1.8 g (85%) of 4 as green crystals. Anal. Found: C, 39.94; H, 3.40. C$_{11}$H$_{11}$Cl$_3$O$_2$Ti. Calc.: C, 40.10; H, 3.37%. ^1H NMR (CDCl$_3$): δ 7.20 (2H, d, H$_{1,3}$); 7.03 (1H, t, H$_2$); 6.64 (2H, s, H$_{5,6}$); 3.96 (6H, s, OCH$_3$).

2.3. 3-Methoxy-1-trimethylsilylindene (5)

A solution of 3-methoxyindene (3.3 g, 22 mmol) in 75 ml of hexane was cooled to 0 °C and 1.6 M butyllithium (14 ml, 22 mmol) was added via a syringe. The reaction mixture was stirred for 8 h at room temperature. The solvent was removed under reduced pressure, and the solid was dissolved in 75 ml of THF. The solution was cooled to 0 °C and chlorotrimethylsilane (2.7 g, 25 mmol) was added. The reaction mixture was stirred overnight, the solvent removed under reduced pressure and the residue was dissolved in 100 ml of

pentane. The suspension was filtered and the solution was concentrated to 1/4 its original volume. Cooling to −20 °C resulted in 4.0 g (83%) of 5 as colorless needles, m.p. 45–46 °C. Anal. Found: C, 71.47; H, 8.28. C$_{13}$H$_{18}$OSi. Calc.: C, 71.50; H, 8.31%. ^1H NMR (CDCl$_3$): δ 7.41–7.22 (4H, m, H$_{4,5,6,7}$); 5.43 (1H, d, H$_2$); 3.88 (3H, s, OCH$_3$); 3.28 (1H, d, H$_1$); −0.04 (9H, s, SiMe$_3$).

2.4. (2-Methoxyethyl)trimethylsilylcyclopentadiene (6)

(2-Methoxyethyl)cyclopentadiene (3.2 g, 26 mmol) was dissolved in 100 ml of hexane, the solution was cooled to 0 °C and 1.6 M butyllithium (16.3 ml, 26 mmol) was added via a syringe. The reaction mixture was stirred for 4 h at room temperature, after which the mixture was cooled to 0 °C. Chlorotrimethylsilane (3.1 g, 29 mmol) was added and the mixture was stirred overnight. The suspension was filtered and the hexane was removed in vacuo to give 3.5 g (69%) of 6 as a yellow oil. ^1H NMR (CDCl$_3$): δ 6.70–6.05 (3H, br m, ring sp^2); 3.55 (2H, t, β-CH$_2$); 3.36 (3H, s, OCH$_3$); 3.01 (1H, br m, ring sp^3); 2.72 (2H, t, α-CH$_2$); −0.09 (9H, s, SiMe$_3$).

2.5. (η^5-(2-Methoxyethyl)cyclopentadienyl)trichlorotitanium (2)

A solution of 6 (3.5 g, 18 mmol) in 100 ml of toluene was cooled to 0 °C and TiCl$_4$ (3.4 g, 18 mmol) was added via a syringe. The reaction mixture was stirred at 0 °C for 30 min and at room temperature for 8 h. After removing the toluene, the solid was dissolved in 75 ml of CH$_2$Cl$_2$ and the mixture was filtered. The solution was concentrated to 1/4 its original volume and cooled to −20 °C to give 4.0 g (80%) of 2 as orange crystals. The physical and spectral data were identical with values given in the literature [6].

2.6. 3-(2-Methoxyethyl)indene (7)

A solution of indene (12.3 g, 0.11 mol) in 150 ml of THF was cooled to 0 °C and 1.6 M butyllithium (66.3 ml, 0.11 mol) was added. After stirring for 6 h at room temperature, (2-chloroethyl) methyl ether (10 g, 0.11 mol) was added dropwise at 0 °C and the mixture was stirred overnight at room temperature. The reaction mixture was hydrolyzed with aqueous NH$_4$Cl and the organic layer was separated, washed with water, dried (Na$_2$SO$_4$) and the solvent evaporated. The residue was vacuum distilled at 80 °C/0.01 mm Hg to give 15.2 g (79%) of 7 as a colorless oil. Anal. Found: C, 82.90; H, 8.07. C$_{12}$H$_{14}$O. Calc.: C, 82.72; H, 8.10%. ^1H NMR (CDCl$_3$): δ 7.32–7.21 (4H, m, H$_{4,5,6,7}$); 6.30 (1H, m, H$_2$); 3.75 (2H, t, β-CH$_2$); 3.36 (3H, s, OCH$_3$); 3.32 (1H, d, ring CH$_2$); 2.83 (2H, br t, α-CH$_2$).

2.7. 3-(2-Methoxyethyl)-1-trimethylsilylindene (8)

To a solution of 7 (4.1 g, 24 mmol) in 100 ml of THF was added 1.6 M butyllithium (14.7 ml, 24 mmol) at 0 °C, and the reaction mixture was warmed to room temperature and stirred for 8 h. Chlorotrimethylsilane (2.8 g, 26 mmol) was slowly added via a syringe at 0 °C and the mixture was stirred at room temperature overnight. The volatiles were removed under reduced pressure and the residue was dissolved in 100 ml of pentane. The suspension was filtered and the pentane removed to give 4.2 g (71%) of 8 as a yellow oil. ^{1}H NMR (CDCl$_3$): δ 7.48–7.26 (4H, m, H$_{4,5,6,7}$); 6.44 (1H, br m, H$_2$); 3.73 (2H, t, β-CH$_2$); 3.47 (1H, br d, ring sp^3); 3.44 (3H, s, OCH$_3$); 2.97 (3H, br t, α-CH$_2$); −0.04 (9H, s, SiMe$_3$).

2.8. η^5-1-(2-Methoxyethyl)indenyltrichlorotitanium (9)

A solution of 8 (4.2 g, 17 mmol) in 75 ml of CH$_2$Cl$_2$ was cooled to −78 °C in a dry-ice–acetone bath. TiCl$_4$ (1.9 g, 17 mmol) was added slowly via a syringe and the solution was stirred for 30 min. The reaction mixture was allowed to warm to room temperature and stirred overnight. The volatiles were removed under reduced pressure, fresh CH$_2$Cl$_2$ (75 ml) was added, and the mixture was filtered. Concentration of the solution to 1/3 its original volume followed by cooling to −20 °C produced 4.2 g (75%) of 9 as dark-red crystals. Anal. Found: C, 43.76; H, 4.30. C$_{12}$H$_{13}$Cl$_3$OTi. Calc.: C, 44.01; H, 4.00%. ^{1}H NMR (CDCl$_3$): δ 7.87–7.47 (4H, m, H$_{4,5,6,7}$); 7.18–7.03 (2H, m, H$_{2,3}$); 3.82 (2H, t, β-CH$_2$); 3.43 (2H, t, α-CH$_2$); 3.36 (3H, s, OCH$_3$).

2.9. 3-(2-Methoxyphenyl)-1-trimethylsilylindene (10)

3-(2-Methoxyphenyl)indene (3.7 g, 17 mmol) was dissolved in 75 ml of Et$_2$O and 1.6 M butyllithium (10.6 ml, 17 mmol) was added at 0 °C. After the reaction mixture was stirred for 8 h at room temperature, chlorotrimethylsilane (2.0 g, 19 mmol) was added and the solution was stirred overnight. The Et$_2$O was removed under reduced pressure and the residue was extracted with 75 ml of pentane. The suspension was filtered and the pentane removed to give 4.8 g (96%) of 10 as a yellow oil. ^{1}H NMR (CDCl$_3$): δ 7.44–7.02 (8H, m, arom H); 6.69 (1H, d, H$_2$); 3.78 (3H, s, OCH$_3$); 3.63 (1H, d, ring sp^3); −0.03 (9H, s, SiMe$_3$).
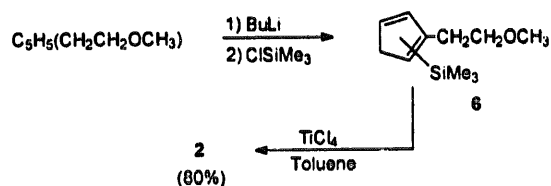
2.10. (η^5 1-(2-Methoxyphenyl)indenyl)trichlorotitanium (11)

To a solution of 10 (4.8 g, 16 mmol) in 75 ml of toluene was added TiCl$_4$ (3.1 g, 16 mmol) at −78 °C. The reaction mixture was warmed to room temperature and stirred overnight. The volatiles were removed under

reduced pressure, the residue was extracted with 75 ml of CH$_2$Cl$_2$, and the mixture was filtered. Concentration of the solution followed by cooling to −20 °C produced 3.8 g (63%) of 11 as dark-blue crystals. Anal. Found: C, 50.77; H, 3.48. C$_{16}$H$_{13}$Cl$_3$OTi. Calc.: C, 51.18; H, 3.49%. ^{1}H NMR (CDCl$_3$): δ 7.86–7.28 (8H, m, H$_{4,5,6,7}$ and phenyl); 7.19–7.00 (2H, m, H$_{2,3}$); 3.86 (3H, s, OCH$_3$).

3. Results and discussion

Since it was found that 1–MAO polymerized ethylene and propylene as well as styrene, we attempted to substitute a harder Lewis base (i.e. oxygen) to determine if a stronger coordination of the pendant group would increase the catalytic activity toward ethylene and propylene. The synthesis of precursor 2 has previously been reported. However, we have prepared 2 by a simpler, alternative synthesis which gave 2 in high yield.

Since Ready and coworkers [11] showed that the use of an indenyl ligand in place of a cyclopentadienyl ligand resulted in higher polymerization activity and stereoselectivity, we have also synthesized [1-(2-methoxyethyl)indenyl]trichlorotitanium (9) in good yield by a similar procedure.
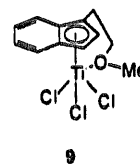
When 2–MAO and 9–MAO were used to polymerize styrene, both catalysts exhibited low activities of ca. 1 × 10^4 g PS/(mol Ti · mol styrene · h), and the syndiotacticity of the PS was greater than 92%. For the polymerization of ethylene, both catalysts also had similar activities of ca. 3 × 10^4 g PE/(mol Ti · [ethylene] · h), although neither catalyst had any activity for propylene polymerization.

In addition to compounds with pendant methoxy substituents, we attempted to synthesize two precursors which contained methoxy substituents directly attached to the indenyl ring. (4,7-Dimethoxyindenyl)trichlorotitanium (4) was prepared in 85% yield from 4,7-dimethoxyindene via the intermediate 4,7-dimethoxy-1-trimethylsilylindene (3).

3   **4**
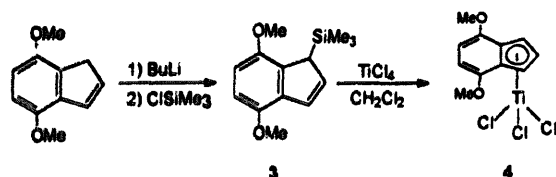
Polymerization of styrene with 4–MAO gave a small amount of *s*-PS with an activity of 2×10^4 g PS/(mol Ti · mol styrene · h). The catalyst 4–MAO had no activity for ethylene or propylene.

Attempts to synthesize (1-methoxyindenyl)trichlorotitanium (12) failed. The conversion of 3-methoxyindene to 3-methoxy-1-trimethylsilylindene (5) went as expected. However, several attempts to convert 5 to 12 using several different solvent systems (e.g. CH_2Cl_2–$TiCl_4$ and toluene–$TiCl_4$) failed to produce 12.


5   **12**
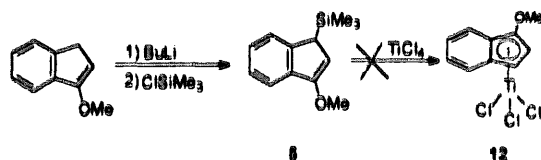
The overall low polymerization activity of the above catalysts could be due to the following factors. One possible factor is oxygen–aluminum coordination between the catalyst and cocatalyst. This coordination has been studied by Piccolrovazzi et al. [7] for methoxy-substituted zirconocenes. The lowering in activity has been attributed to the fact that oxygen–aluminum coordination suppresses the resonance effect and enhances the inductive effects of the methoxy group.

However, there is another possible reason for the lowering in polymerization activity when methoxy-substituted precursors are activated with MAO. Since MAO is a polymeric species, when oxygen–aluminum coordination takes place the amount of steric hindrance around the catalytic center is dramatically increased, which could inhibit monomer coordination and result in lower activity. Furthermore, the oxygen–aluminum coordination could substantially decrease the ability of MAO to

abstract an anionic ligand from titanium to form the cationic organotitanium active species.

In an attempt to minimize the coordination between MAO and the methoxy substituent, we prepared a precursor which would have more steric bulk around the oxygen atom. Accordingly, we synthesized [1-(2-methoxyphenyl)indenyl]trichlorotitanium (11) with the idea that when the oxygen was coordinated to the titanium center, the phenyl ring might prevent coordination of MAO with the oxygen. Unfortunately, no improvement in catalytic activity was observed with 11–MAO.

11
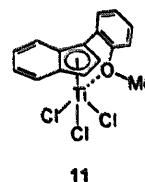
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