Synthesis and polymerization behavior of tetrahydro-2-methylbenzindenyltitanium and zirconium compounds[1]

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Abstract

In order to further our study of the bis(2-methylbenz[e]indenyl)zirconium dichloride catalyst system, we have synthesized the analogous tetrahydro-2-methylbenz[e]indene ligand (**4**). In the process of synthesizing **4**, we have found that the structural isomer tetrahydro-2-methylbenz[f]indene (**5**) is also formed. This has been confirmed by the synthesis of a series of dimethyl (**6** and **7**), methyl-phenyl (**8**), and titanium trichloride derivatives (**11** and **12**) of the parent indenes **4** and **5**. The new ligand systems **4**, **6**, **7**, and **8** were converted to the analogous unbridged zirconocene dichloride complexes **13**, **14**, **15**, and **16**. The precursors were then activated with either methylaluminoxane (MAO) or triphenylcarbenium tetrakis(pentafluorophenyl)borate (trityl) and used as catalysts for the polymerization of ethylene and propylene. All zirconocene complexes were highly active for the polymerization of ethylene, and in some cases produced crystalline polypropylene at lower polymerization temperatures. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

In 1985, Kaminsky et al. [3] reported that use of 4,5,6,7-tetrahydroindene in place of indene in the formation of rac-ethylenebis(η^5-4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride (**1**) produced a catalyst which formed highly isotactic polypropylene (> 91%) when activated with MAO.

The drawback of the catalyst system **1**/MAO is that the polypropylene produced has a very low molecular weight (< 30000), which makes it non-practical for industrial applications [3]. One solution which was found to alleviate the problem of low molecular weight was to use hafnium derivatives in place of zirconium precursors [4]. However, the activity of the hafnium systems was found to be about 5% that of the zirco-

nium analogs [5], making these catalysts financially non-practical.

In 1992, Spaleck et al. [6] reported the synthesis of several new *ansa*-metallocenes in an effort to produce catalysts which exhibited both high activity and high molecular weight. These new catalysts incorporated two important structural features: (1) a dimethylsilylene bridge between the two pentahapto ligands; and (2) a methyl substituent at the C-2 position of the bridged indene. In addition, Spaleck et al. [6,7] and Brintzinger et al. [8] also found that annelation of a benzo ring on an indenyl ligand is an important structural feature for both high molecular weight and high isotacticity.

In a recent study [9], we reported the synthesis of several unbridged bis-benz[e]indenyl metallocene complexes which when activated with methylaluminoxane (MAO) or triphenylcarbenium tetrakis(pentafluorophenyl)borate (trityl) would possibly produce regioregular polypropylene. This phenomenon has recently been reported by Waymouth et al. [10] by using

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[1] See Foster [1] and Schneider et al. [2].

unbridged bis-(η^5-2-phenylindenyl)zirconium dichloride activated with MAO to produce elastomeric polypropylene. Due to the apparent free rotation at all polymerization temperatures studied, our benz[e]indenyl catalyst systems produced only amorphous polypropylene. However, the molecular weight of the polymer produced varied considerably as the polymerization temperature was varied.

Therefore, in the present study we have synthesized a ligand which incorporates many of the above mentioned structural features and also incorporates a tetrahydro C_6 ring which could further hinder free rotation of the two pentahapto ligands. In addition, substitution on the C_5 ring was introduced in order to add further steric hindrance to the catalytic system. Polymerizations were carried using both MAO and trityl as a cocatalyst so that a wide polymerization temperature range could be studied.

2. Experimental section

Reactions were carried out under an argon atmosphere using standard Schlenk techniques. The argon was purified by deoxygenating with BTS catalyst and drying with molecular sieves, calcium chloride, and P_2O_5. Tetrahydrofuran (THF) was predried over sodium wire, distilled from sodium under argon, and finally distilled from Na/K alloy under argon. Diethyl ether was predried over sodium wire and distilled from Na/K alloy under argon. Toluene, hexane, and pentane were distilled from Na/K alloy under argon. Methylene chloride was distilled under argon from calcium hydride.

Methylaluminoxane was purchased from Akzo. All other reagents were purchased from Aldrich and were used without further purification. Celite was purchased from Fisher Scientific and used without pretreatment. ^{1}H-NMR spectra were recorded on a Varian XL-200 or a Bruker NR-80 spectrometer with tetramethylsilane (TMS) as an internal standard. ^{13}C-NMR spectra were recorded on a Bruker MSL-300 spectrometer. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

2.1. Tetrahydro-2-methylbenz[e]indan-1-one and tetrahydro-2-methylbenz[f]indan-1-one (2,3)

To a suspension of $AlCl_3$ (222.96 g, 1.67 mol) in 200 ml of CH_2Cl_2 at 0°C, was added 2-bromoisobutyryl bromide (145.1 g, 0.63 mol) over a 15 min period. Following the addition, the reaction mixture was stirred at 0°C for 45 min and 5,6,7,8-tetrahydronapthalene (83.43 g, 0.63 mol) in 200 ml of CH_2Cl_2 was added dropwise. Once the addition was complete, the reaction mixture was warmed to room temperature (r.t.) and stirred for 5 h. The mixture was slowly poured over ice

and the organic layer was separated. The aqueous layer was extracted with an additional 100 ml of CH_2Cl_2 and the organic layers were combined. The organic extracts were dried with $MgSO_4$, the suspension filtered, and the solvent removed. The residue was vacuum distilled (135–140°C/0.01 mmHg) to give 99.72 g (79%) of a mixture of **2** and **3** as a yellow liquid which crystallized upon standing at r.t. Recrystallization of the distillate from pentane gave **2** (58.45 g) as colorless crystals, m.p. 80–81°C. Anal. Found: C, 83.73; H, 8.06. $C_{14}H_{16}O$. Anal. Calc.: C, 83.96; H, 8.05%. ^{1}H-NMR (CDCl$_3$):δ 7.51 (d, 1H, aromatic H); 7.08 (d, 1H, aromatic H); 3.23–3.15 (m, 1H, C_5–CH); 2.86–2.81 (m, 2H, C_6-α-CH$_2$); 2.77–2.61 (m, 2H, C_6-α-CH$_2$); 2.53 (dd, 2H, C_5–CH$_2$); 1.88–1.78 (m, 4H, C_6-β-CH$_2$); 1.29 (d, 3H, CH$_3$).

After filtration of the above crystals, the solvent was removed from the filtrate to give **3** (36.80 g) as a yellow liquid. ^{1}H-NMR (CDCl$_3$): δ 7.47 (s, 1H, aromatic H); 7.15 (s, 1H, aromatic H); 3.40–3.26 (m, 1H, C_5–CH); 2.85–2.80 (m, 2H, C_6-α-CH$_2$); 2.71–2.60 (m, 4H, C_6-α-CH$_2$ and C_5–CH$_2$); 1.84–1.78 (m, 4H, C_6-β-CH$_2$); 1.30 (d, 3H, CH$_3$).

2.2. Tetrahydro-2-methylbenz[e]indene (4)

A solution of **2** (10.10 g, 50 mmol) in 150 ml of THF was cooled to 0°C, and 3.4 M NaAlH$_2$(OCH$_2$CH$_2$OCH$_3$)$_2$ (18.0 ml, 60 mmol) in toluene was added dropwise. After the addition was complete, the mixture was warmed to r.t. and stirred overnight. The reaction mixture was hydrolyzed by slow addition of 15 ml of 10% aqueous HCl. The resulting suspension was filtered and the filtrate was dried with $MgSO_4$. The solvent was removed to give 8.65 g (85.6%) of the crude tetrahydro-2-methylbenz[e]indanol as a white solid. The alcohol was used in the next step without further purification.

The crude tetrahydro-2-methylbenz[e]indanol (8.65 g, 43 mmol) was dissolved in 200 ml of toluene and 9.0 g of oxalic acid was added. The reaction mixture was refluxed for 4 h while the water produced was separated using a Dean-Stark trap. The mixture was cooled to r.t. and the excess oxalic acid was neutralized by addition of 150 ml of 15% NaHCO$_3$. The organic layer was separated, and the aqueous layer was extracted with an additional 100 ml of toluene. The combined organic layers were dried with $MgSO_4$ and the solvent was removed. The residue was crystallized from pentane at −20°C to give 6.42 g (81%) of **4** as colorless crystals, m.p. 30–31°C. Anal. Found: C, 91.31; H, 8.94. $C_{14}H_{16}$. Anal. Calc.: C, 91.25; H, 8.75%. ^{1}H-NMR (CDCl$_3$): δ 7.15–6.80 (m, 2H, aromatic H); 6.43 (br s, 1H, C_5-sp^2); 3.09 (s, 2H, C_5–CH$_2$); 2.82–2.76 (m, 2H, C_6-α-CH$_2$); 2.69–2.66 (m, 2H, C_6-α-CH$_2$); 2.14 (s, 3H, CH$_3$); 1.84–1.80 (m, 4H, C_6-β-CH$_2$).

2.3. Tetrahydro-2-methylbenz[f]indene (5)

A solution of **3** (34.30 g, 171.3 mmol) in 150 ml of THF was cooled to 0°C, and 3.4 M $NaAlH_2(OCH_2CH_2OCH_3)_2$ (60.5 ml, 206 mmol) in toluene was added dropwise. After the addition was complete, the mixture was warmed to r.t. and stirred overnight. The reaction mixture was hydrolyzed by slow addition of 15 ml of 10% aqueous HCl. The resulting suspension was filtered and the filtrate was dried with $MgSO_4$. The solvent was removed to give 28.24 g (81.5%) of the crude tetrahydro-2-methyl-benz[f]indanol as a white solid. The alcohol was used in the next step without further purification.

The crude tetrahydro-2-methylbenz[f]indanol (28.24 g, 140 mmol) was dissolved in 200 ml of toluene and 29.38 g of oxalic acid was added. The reaction mixture was refluxed for 4 h while the water produced was separated using a Dean-Stark trap. The mixture was cooled to r.t. and the excess oxalic acid was neutralized by addition of 150 ml of 15% $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted with an additional 100 ml of toluene. The combined organic layers were dried with $MgSO_4$ and the solvent was removed. The residue was crystallized from pentane at $-20°C$ to give 18.67 g (72.6%) of **5** as colorless crystals. ^1H-NMR ($CDCl_3$): δ 7.04 (s, 1H, aromatic H); 6.92 (s, 1H, aromatic H); 6.37 (s, 1H, C_5-sp^2); 3.20 (s, 2H, C_5–CH_2); 2.79–2.73 (m, 4H, C_6-α-CH_2); 2.10 (s, 3H, CH_3); 1.81–1.75 (m, 4H, C_6-β-CH_2).

2.4. Tetrahydro-2,3-dimethylbenz[f]indene (6)

A solution of **3** (11.5 g, 57 mmol) in 200 ml of THF was cooled to 0°C and 3.0 M CH_3MgBr (21.0 ml, 63 mmol) in diethyl ether was added dropwise. The reaction mixture was warmed to r.t. and stirred for 4 h. Following 2 h of reflux, the mixture was cooled to r.t. and 200 ml of saturated aqueous NH_4Cl was added. The organic layer was separated and the aqueous layer was extracted with 100 ml of diethyl ether. The combined organic layers were dried with $MgSO_4$, filtered and the solvent was removed.

The residue was dissolved in 200 ml of toluene and 12 g of oxalic acid was added. The mixture was refluxed for 2 h while the water produced was separated using a Dean-Stark trap. The solution was cooled to r.t. and 200 ml of 15% aqueous $NaHCO_3$ was slowly added. The organic layer was separated and the aqueous layer was extracted with an additional 100 ml of toluene. The combined organic layers were dried with $MgSO_4$, filtered, and the solvent removed. The residue was vacuum distilled at 149–151°C/0.01 mm Hg to give 7.20 g (64%) of **6** as a colorless liquid. Anal. Found: C, 90.92; H, 9.12. $C_{15}H_{18}$. Anal. Calc.: C, 90.85; H, 9.15%. ^1H-NMR ($CDCl_3$): δ 7.05 (s, 1H, aromatic H); 6.89 (s, 1H, aromatic H); 3.18 (s, 2H, C_5–CH_2); 2.81–2.78 (br m, 4H, C_6-α-CH_2); 2.02 (s, 3H, CH_3); 1.98 (s, 3H, CH_3); 1.83–1.76 (m, 4H, C_6-β-CH_2).

2.5. Tetrahydro-2,3-dimethylbenz[e]indene (7)

A solution of **2** (10.0 g, 50 mmol) in 200 ml of THF was cooled to 0°C and 3.0 M CH_3MgBr (18.3 ml, 55 mmol) in diethyl ether was added dropwise. The reaction mixture was warmed to r.t. and stirred for 4 h. Following 2 h of reflux, the mixture was cooled to r.t. and 200 ml of saturated aqueous NH_4Cl was added. The organic layer was separated and the aqueous layer was extracted with 100 ml of diethyl ether. The combined organic layers were dried with $MgSO_4$, filtered and the solvent was removed.

The residue was dissolved in 200 ml of toluene and 10.5 g of oxalic acid was added. The mixture was refluxed for 2 h while the water produced was separated using a Dean-Stark trap. The solution was cooled to r.t. and 200 ml of 15% aqueous $NaHCO_3$ was slowly added. The organic layer was separated and the aqueous layer was extracted with an additional 100 ml of toluene. The combined organic layers were dried with $MgSO_4$, filtered, and the solvent removed. The residue was recrystallized from pentane to give 6.45 g (65%) of **7** as colorless crystals, m.p. 79–81°C. An analytical sample was obtained by vacuum sublimation (75°C/0.01 mmHg) of the crystallized product. Anal. Found: C, 90.52; H, 9.35. $C_{15}H_{18}$. Anal. Calc.: C, 90.85; H, 9.15%. ^1H-NMR ($CDCl_3$): δ 7.00 (s, 2H, aromatic H); 3.07 (br s, 2H, C_5–CH_2); 2.81–2.78 (m, 2H, C_6-α-CH_2); 2.71–2.68 (m, 2H, C_6-α-CH_2); 2.05 (s, 3H, CH_3); 2.00 (s, 3H, CH_3); 1.86–1.80 (m, 4H, C_6-β-CH_2).

2.6. Tetrahydro-2-methyl-3-phenylbenz[e]indene (8)

To a suspension of magnesium turnings (1.82 g, 75 mmol) in a mixture of 50 ml of THF and 50 ml of diethyl ether was slowly added bromobenzene (11.78 g, 75 mmol) and the mixture was stirred for 2 h. A solution of **2** (15.0 g, 75 mmol) in a mixture of 100 ml of THF and 100 ml of diethyl ether was added dropwise and the reaction mixture was stirred overnight. The white suspension was added to 200 ml of saturated aqueous NH_4Cl and the organic layer was extracted. The aqueous layer was extracted with an additional 100 ml of diethyl ether and the organic layers were combined. After drying with $MgSO_4$, the solution was filtered and the solvent removed to give the crude alcohol (19.36 g, 93%) as a white solid.

The crude alcohol (19.36 g, 70 mmol) was dissolved in 300 ml of toluene and 20 g of oxalic acid was added. The reaction mixture was refluxed for 5 h while the water produced was separated using a Dean-Stark trap. The solution was cooled to r.t. and the excess oxalic

acid was neutralized by the slow addition of 300 ml of 15% $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with an additional 100 ml of toluene. The combined organic layers were dried with $MgSO_4$, filtered, and the solvent removed. The residue was recrystallized from pentane to give 10.66 g (55%) of **8** as colorless crystals, m.p. 77–79°C. Anal. Found: C, 91.90; H, 7.72. $C_{20}H_{20}$. Anal. Calc.: C, 92.26; H, 7.74%. ^{1}H-NMR (CDCl$_3$): δ 7.45–7.32 (m, 5H, phenyl); 7.01 (m, 1H, aromatic H); 7.00 (m, 1H, aromatic H); 3.28 (s, 2H, C$_5$–CH$_2$); 2.85-2.73 (m, 4H, C$_6$-α-CH$_2$); 2.14 (s, 3H, CH$_3$); 1.89–1.82 (m, 4H, C$_6$-β-CH$_2$).

2.7. Tetrahydro-2-methyl-1-(trimethylsilyl)-benz[e]-indene (9)

A solution of **4** (3.00 g, 16 mmol) in 100 ml of THF was cooled to 0°C and 1.6 M butyllithium in hexane (10.2 ml, 16 mmol) was slowly added. The reaction mixture was warmed to r.t. and stirred for 4 h to give an orange–red solution. The solution was cooled to 0°C and chlorotrimethylsilane (1.96 g, 18 mmol) was added. The mixture was warmed to r.t. and stirred overnight. The solvent was removed and the residue was extracted with 75 ml of pentane. The suspension was filtered and the pentane was removed in vacuo to give 4.04 g (98%) of **9** as a yellow liquid. ^{1}H-NMR (CDCl$_3$): δ 7.10 (d, 1H, aromatic H); 6.81 (d, 1H, aromatic H); 6.58 (s, 1H, C$_5$-sp^2); 3.28 (s, 1H, C5-sp^3); 2.83–2.79 (m, 4H, C$_6$-α-CH$_2$); 2.20 (s, 3H, CH$_3$); 1.86–1.79 (m, 4H, C$_6$-β-CH$_2$); -0.01 (s, 9H, SiMe$_3$).

2.8. Tetrahydro-2-methyl-1-(trimethylsilyl)-benz[f]-indene (10)

A solution of **5** (1.50 g, 8.0 mmol) in 100 ml of THF was cooled to 0°C and 1.6 M butyllithium in hexane (5.0 ml, 8.0 mmol) was slowly added. The reaction mixture was warmed to r.t. and stirred for 4 h to give an orange–red solution. The solution was cooled to 0°C and chlorotrimethylsilane (0.87 g, 8.0 mmol) was added. The mixture was warmed to r.t. and stirred overnight. The solvent was removed and the residue was extracted with 50 ml of pentane. The suspension was filtered and the pentane was removed in vacuo to give 1.83 g (89%) of **10** as colorless crystals, m.p. 67–68°C. Anal Found: C, 79.59; H, 9.36. $C_{17}H_{24}Si$. Anal. Calc.: C, 79.62; H, 9.43%. ^{1}H-NMR (CDCl$_3$): δ 6.91 (s, 1H, aromatic H); 6.89 (s, 1H, aromatic H); 6.34 (s, 1H, C$_5$-sp^2); 3.11 (s, 1H, C$_5$–CH); 2.70 (m, 4H, C$_6$-α-CH$_2$); 2.06 (s, 3H, CH$_3$); 1.72–1.69 (m, 4H, C$_6$-β-CH$_2$); -0.096 (s, 9H, SiMe$_3$).

2.9. (η^5-Tetrahydro-2-methylbenz[e]indenyl)titanium trichloride (11)

A solution of **9** (4.04 g, 16 mmol) in 75 ml of CH$_2$Cl$_2$ was cooled to 0°C and TiCl$_4$ (3.00 g, 16 mmol) was added. The reaction mixture was warmed to r.t. and stirred for 5 h. The solvent was removed, and the residue was extracted with 50 ml of toluene. After filtration, 10 ml of hexane was added and the mixture was cooled to -78°C to give 3.20 g (59%) of **11** as red crystals. Anal. Found: C, 50.07; H, 4.56. $C_{14}H_{15}Cl_3Ti$. Anal. Calc.: C, 49.82; H, 4.48%. ^{1}H-NMR (CDCl$_3$): δ 7.48 (d, 1H, aromatic H); 7.19 (d, 1H, aromatic H); 6.98 (br s, 1H, C$_5$–H); 6.89 (br s, 1H, C$_5$–H); 3.20–2.86 (br m, 4H, C$_6$-α-CH$_2$); 2.65 (s, 3H, CH$_3$); 1.94–1.85 (br m, 4H, C$_6$-β-CH$_2$).

2.10. (η^5-Tetrahydro-2-methylbenz[f]indenyl)titanium trichloride (12)

A solution of **10** (1.83 g, 7.1 mmol) in 75 ml of CH$_2$Cl$_2$ was cooled to 0°C and TiCl$_4$ (1.35 g, 7.1 mmol) was added. The reaction mixture was warmed to r.t. and stirred for 5 h. The solvent was removed, and the residue was extracted with 50 ml of hexane. After filtration, the mixture was concentrated and cooled to -20°C to give 1.10 g (46%) of **12** as red crystals. ^{1}H-NMR (CDCl$_3$): δ 7.47 (s, 2H, aromatic H); 6.91 (s, 2H, C$_5$–H); 2.96–2.93 (m, 4H, C$_6$-α-CH$_2$); 2.59 (s, 3H, CH$_3$); 1.86–1.83 (m, 4H, C$_6$-β-CH$_2$).

2.11. Bis(η^5-tetrahydro-2-methylbenz[e]indenyl)-zirconium dichloride (13)

A solution of **4** (2.50 g, 14 mmol) in a mixture of 50 ml of THF and 40 ml of diethyl ether was cooled to 0°C and 1.6 M butyllithium in hexane (8.75 ml, 14 mmol) was added. The reaction mixture was warmed to r.t. and stirred for 5 h. The solution was cooled to 0°C and added to a suspension of ZrCl$_4$ (1.63 g, 7.0 mmol) in a mixture of 30 ml of THF and 30 ml of diethyl ether at -78°C. The reaction mixture was warmed to r.t. and stirred overnight. The suspension was filtered and the solvent was removed. The residue was extracted with toluene and cooled to -20°C to give a 1:1 mixture of *rac*-like and *meso*-like isomers of **13** (2.26 g, 61%) as an orange solid. Anal. Found: C, 63.07; H, 5.77; Cl, 13.92. $C_{28}H_{30}Cl_2Zr$. Anal. Calc.: C, 63.61; H, 5.72; Cl, 13.41%. ^{1}H-NMR (CD$_2$Cl$_2$): *rac*-like: δ 6.97 (d, 2H, aromatic H); 6.79 (d, 2H, aromatic H); 6.05 (d, 2H, C$_5$–H); 5.80 (d, 2H, C$_5$–H); 2.91–2.68 (m, 8H, C$_6$-α-CH$_2$); 1.96 (s, 6H, CH$_3$); 1.87–1.83 (m, 8H, C$_6$-β-CH$_2$). *meso*-like: δ 7.41 (d, 2H, aromatic H); 7.18 (d, 2H, aromatic H); 6.22 (br s, 2H, C$_5$–H); 6.15 (br s, 2H, C$_5$–H); 2.88–2.68 (m, 8H, C$_6$-α-CH$_2$); 2.13 (s, 6H, CH$_3$); 1.86–1.83 (m, 8H, C$_6$-β-CH$_2$).

2.12. Bis(η^5-tetrahydro-2,3-dimethylbenz[f]indenyl)-zirconium dichloride (14)

A solution of 6 (2.03 g, 10 mmol) in a mixture of 50 ml of THF and 50 ml of diethyl ether was cooled to 0°C and 1.6 M butyllithium in hexane (6.4 ml, 10 mmol) was slowly added. The mixture was warmed to r.t. and stirred for 4 h. The red–orange solution was cooled to 0°C and added via cannula to a suspension of ZrCl₄ (1.16 g, 5.0 mmol) in a mixture of 25 ml of THF and 25 ml of diethyl ether at −78°C. The mixture was warmed to r.t. and stirred overnight. The solvent was removed and the residue was extracted with 30 ml of toluene. Following filtration, the solution was cooled to −20°C to give 1.82 g (65%) of a 1:2 mixture of *rac*-like and *meso*-like isomers of 14 as an orange solid. Anal. Found: C, 64.14; H, 6.32. $C_{30}H_{34}Cl_2Zr$. Anal. Calc.: C, 64.72; H, 6.16%. ^{1}H-NMR (CDCl₃): *rac*-like: δ 7.34 (s, 2H, aromatic H); 7.25 (s, 2H, aromatic H); 5.52 (s, 2H, C₅–H); 2.90–2.83 (br m, 8H, C₆-α-CH₂); 2.22 (s, 3H, CH₃); 1.82–1.78 (m, 8H, C₆-β-CH₂); 1.71 (s, 3H, CH₃). *meso*-like: δ 7.17 (s, 2H, aromatic H); 6.96 (s, 2H, aromatic H); 5.61 (s, 2H, C₅–H); 2.90–2.83 (br m, 8H, C₆-α-CH₂); 2.14 (s, 3H, CH₃); 2.05 (s, 3H, CH₃); 1.83–1.78 (m, 8H, C₆-β-CH₂).

2.13. Bis(η^5-tetrahydro-2,3-dimethylbenz[e]indenyl)-zirconium dichloride (15)

A solution of 7 (2.29 g, 11.5 mmol) in an mixture of 40 ml of THF and 40 ml of diethyl ether was cooled to 0°C and 1.6 M butyllithium in hexane (7.2 ml, 11.5 mmol) was slowly added. The solution was warmed to r.t. and stirred for 5 h. The reaction mixture was again cooled to 0°C and added via a cannula to a suspension of ZrCl₄ (1.35 g, 5.8 mmol) in a mixture of 20 ml of THF and 20 ml of diethyl ether at −78°C. The mixture was warmed to r.t. and stirred overnight. The solvent was removed in vacuo and the residue was extracted with 35 ml of toluene. Following filtration, the solution was cooled to −20°C to give 1.95 g (60%) of 15 as orange crystals. Anal. Found: C, 64.81; H, 6.03. $C_{30}H_{34}Cl_2Zr$. Anal. Calc.: C, 64.72; H, 6.16%. ^{1}H-NMR (CDCl₃): δ 7.23 (d, 2H, aromatic H); 6.92 (d, 2H, aromatic H); 5.78 (s, 2H, C₅–H); 2.70–2.37 (m, 8H, C₆-α-CH₂); 2.28 (s, 3H, CH₃); 2.23 (s, 3H, CH₃); 1.85–1.78 (m, 8H, C₆-β-CH₂).

2.14. Bis(η^5-tetrahydro-2-methyl-3-phenylbenz[e]-indenyl)zirconium dichloride (16)

A solution of 8 (2.24 g, 8.6 mmol) in a mixture of 40 ml of THF and 40 ml of diethyl ether was cooled to 0°C and 1.6 M butyllithium (5.4 ml, 8.6 mmol) was slowly added. The mixture was warmed to r.t. and stirred for 4 h. The solution was again cooled to 0°C and added via a cannula to a suspension of ZrCl₄ (1.00 g, 4.3 mmol) in a mixture of 25 ml of THF and 25 ml of diethyl ether at −78°C. The reaction mixture was warmed to r.t. and stirred overnight. The solvent was removed and the residue was extracted with 35 ml of toluene. Following filtration, the solution was concentrated to a quarter its original volume and 5 ml of hexane was added. The mixture was cooled to −20°C to give 1.65 g (52%) of 16 as orange crystals. Anal. Found: C, 72.30; H, 5.94. $C_{40}H_{38}Cl_2Zr \cdot 2/3C_7H_8$. Anal. Calc.: C, 72.28; H, 5.88%. ^{1}H-NMR (CDCl₃): δ 7.62 (d, 2H, aromatic H); 7.46–7.18 (m, 10H, phenyl); 7.03 (d, 2H, aromatic H); 5.85 (s, 2H, C₅–H); 2.96–2.75 (br m, 8H, C₆-α-CH₂); 2.35 (s, 2H, C₇H₈); 1.98 (s, 3H, CH₃); 1.90–1.85 (br m, 8H, C₆-β-CH₂).

2.15. Polymerization procedure with MAO cocatalyst

A 250 ml glass pressure bottle was sealed under a nitrogen atmosphere. Freshly distilled toluene (50 ml) was added via a syringe, and pressurized with ethylene or propylene (15 psi) and the appropriate amount of methylaluminoxane (MAO). The bottle was placed in a bath at the desired polymerization temperature and stirred for 10 min. The catalyst precursor in toluene was then added, and the mixture was stirred until the desired reaction time was reached. The reaction mixture was subsequently quenched with 10% HCl in methanol, filtered, and dried in a vacuum at 70°C.

2.16. Polymerization procedure with trityl cocatalyst

A 250 ml glass pressure bottle was sealed under a nitrogen atmosphere. Freshly distilled toluene (50 ml) was added via a syringe, and pressurized with ethylene or propylene (15 psi) and the appropriate amount of triisobutylaluminum (TIBA). The bottle was placed in a bath at the desired polymerization temperature and stirred for 10 min. The catalyst precursor in toluene was then added and the solution was stirred for 5 min. Triphenylcarbenium tetrakis(pentafluorophenyl)borate in toluene was added and the mixture was stirred until the desired reaction time was reached. The reaction mixture was subsequently quenched with 10% HCl in methanol, filtered, and dried in a vacuum at 70°C.
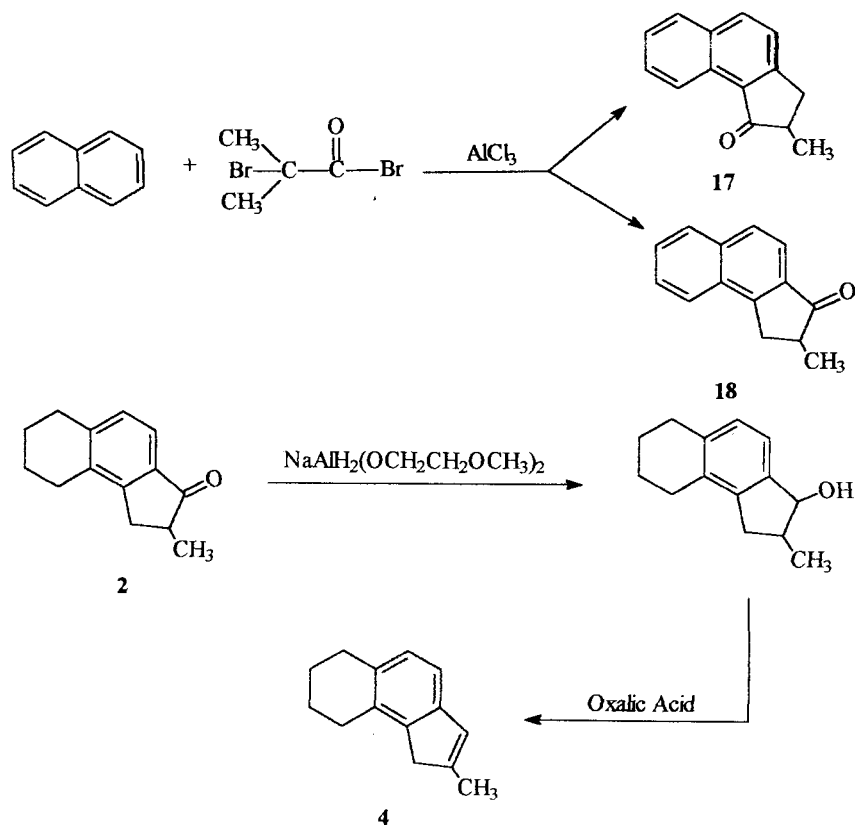
2.17. Polymer analysis

Molecular weights were determined by intrinsic viscosity in 1,3,5-trichlorobenzene at 135°C. Melting points were determined with a Perkin-Elmer DSC-4 system at a heating rate of 20°C min⁻¹.

3. Results and discussion

3.1. Synthesis of tetrahydro-2-methylbenz[e]indenyl and tetrahydro-2-methylbenz[f]indenyl ligands

It has been shown that the reaction of naphthalene with 2-bromoisobutyryl bromide in the presence of $AlCl_3$ produces a mixture of two isomeric ketones **17** and **18** [8]. The mixture of isomers **17** and **18** was not separated and was used to produce 2-methyl-benz[e]indene as a mixture of isomers.

mixture of ketones **2** and **3** in 79% combined yield. It was originally thought that the reaction produced two different benz[e]indanone isomers, however subsequent structural and derivative studies confirmed the presence of two different structural isomers, **2** and **3**. These structures were also confirmed by the work of Brintzinger et al. [2].

In contrast to ketones **17** and **18**, separation of the two isomeric ketones **2** and **3** was accomplished by recrystallization from pentane, giving compound **3** as a

Since the above reaction proceeds in fairly high yield (74%), a different aromatic substrate was used in order to produce an alternative ligand system. The reaction of 1,2,3,4-tetrahydronaphthalene with 2-bromoisobutyryl bromide in the presence of $AlCl_3$ also produced a 40:60

yellow liquid and compound **2** as colorless crystals. Compound **2** was then reduced using $NaAlH_2(OCH_2CH_2OCH_3)_2$ followed by dehydration with oxalic acid to give tetrahydro-2-methyl-benz[e]indene (**4**) in 81% yield.
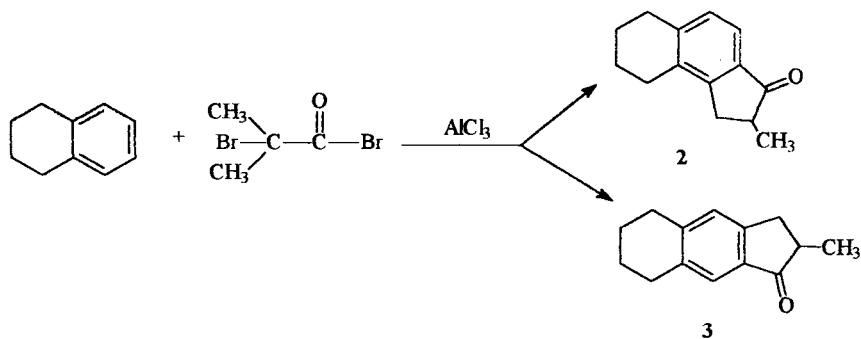
In a similar fashion the ketone **3** was reduced using NaAlH$_2$(OCH$_2$CH$_2$OCH$_3$)$_2$ followed by dehydration with oxalic acid to give tetrahydro-2-methyl-benz[*f*]indene (**5**) in 72.6% yield.

5
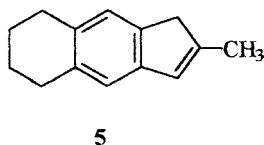
The ^{1}H-NMR spectra of compounds **4** and **5** show two different splitting patterns for the aromatic protons on the C$_6$ ring. In compound **4** the aromatic protons appear as two sets of doublets since the two aromatic protons are coupled to each other, while in compound **5** the two aromatic protons appear as two singlets since there are no adjacent protons.

In order to further characterize the structures of the two isomeric ketones **2** and **3**, a series of methyl and phenyl derivatives were synthesized. Two dimethyl derivatives **6** and **7** were synthesized by reaction of the appropriate ketone with CH$_3$MgBr followed by oxalic acid dehydration of the corresponding alcohol to give tetrahydro-2,3-dimethylbenz[*f*]indene (**6**) and tetrahydro-2,3-dimethylbenz[*e*]indene (**7**) in 64 and 65% yield, respectively. The ^{1}H-NMR spectra of the two compounds **6** and **7** was used to assist in assigning the structures of the two isomeric ketones **2** and **3**. As expected, the aromatic region of the ^{1}H-NMR spectra of compounds **6** and **7** show different splitting patterns for the two protons on the aromatic C$_6$ ring. In the case of compound **6**, the aromatic region consists of two singlets at 6.89 and 7.05 ppm, while for compound **7** the two aromatic protons appear as one singlet at 7.00 ppm.

The difference in the splitting pattern in the two spectra is directly related to the position of the C$_5$ ring on the aromatic C$_6$ ring. For compound **6** the two aromatic protons appear as two distinct singlets due to the fact that there are no adjacent protons to the two aromatic protons in the benz[*f*]indene type system. In the case of compound **7**, the two aromatic protons appear as one singlet which was troubling since we expected to see the aromatic protons appear as two doublets as seen in compounds **2** and **4**. In order to determine if the equivalence was due to the methyl substituent at the C-3 position the methyl group was changed to a phenyl group.

Compound **8** was synthesized by reaction of ketone **2** with PhMgBr followed by oxalic acid to give tetrahydro-2-methyl-3-phenylbenz[*e*]indene (**8**) in 55% yield. In this case, the two aromatic protons appear as a distorted AB quartet due to the non-equivalence of the protons.


2

2a
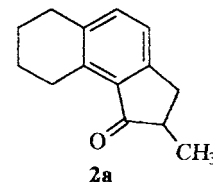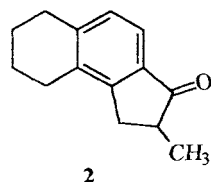
3.2. Synthesis of Group 4 organometallic complexes of the substituted tetrahydro-2-methylbenz[e]indenes

In order to further confirm the structure of ketones **2** and **3**, the half-sandwich titanium trichloride complexes of ligands **4** and **5** were synthesized. If the reaction of tetrahydronaphthalene with 2-bromoisobutyryl
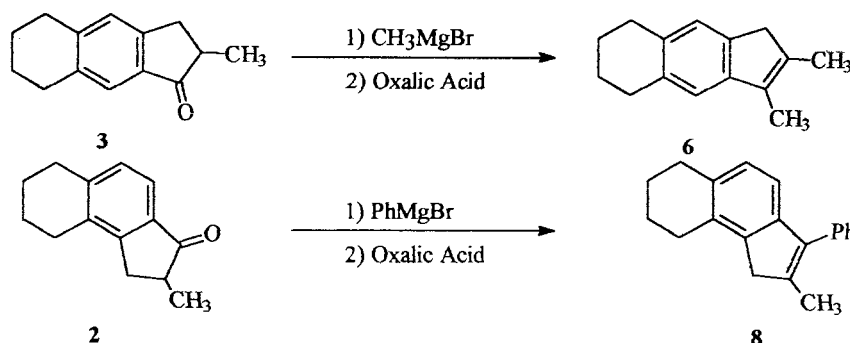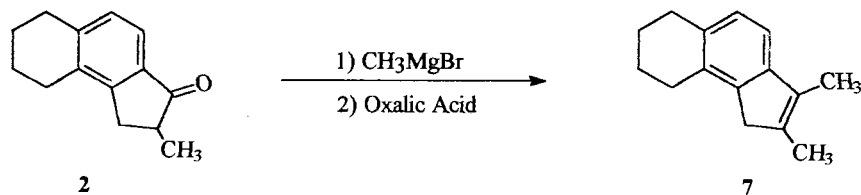
bromide gives two benz[e]indanone isomers **2** and **2a**, then subsequent formation of the corresponding indene derivatives followed by conversion to the titanium trichloride derivatives should give identical products.
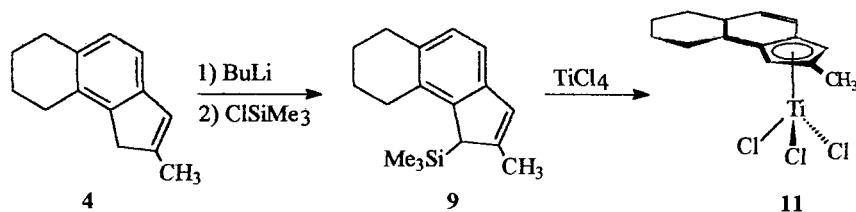
Conversely, if the product of the above reaction is one benz[e]indanone and one benz[f]indanone isomer then subsequent reaction to the titanium trichloride derivatives should give two different products. Reaction of tetrahydro-2-methylbenz[e]indene (**4**) with butyllithium followed by ClSiMe₃ produced the trimethylsilyl derivative **9** in 98% yield. Subsequent reaction of **9** with TiCl₄ in dichloromethane gave (η^5-tetrahydro-2-methyl-benz[e]indenyl)titanium trichloride (**11**) in 59% yield.

Likewise, when **5** was reacted as described for **4**, a different product was obtained which corresponds to the 2-methylbenz[f]indenyltitanium trichloride (**12**). Therefore, we can conclude that the reaction between tetrahydronaphthalene and 2-bromoisobutyryl bromide gives ketones **2** and **3** as the products.

In addition to the titanium complex above, un-bridged zirconocene complexes of ligands **4**, **6**, **7**, and **8** were also prepared. Reaction of compound **4** with butyllithium in a mixture of THF and diethyl ether followed by reaction with ZrCl₄ gave compound **13** in 61% yield. The product, bis(η^5-tetrahydro-2-methyl-benz[e]indenyl)zirconium dichloride (**13**), was obtained as a mixture of two isomers. Both the 'meso-like' and 'rac-like' isomers were obtained in a 1:1 mixture which could not be separated by crystallization due to the high degree of solubility of both isomers in organic solvents.

Compounds **14** and **15** were synthesized by procedures similar to that used for the synthesis of compound **13**. Compound **14** was also isolated as a 1:2 mixture of 'rac-like' and 'meso-like' isomers in 65% yield. The ¹H-NMR spectrum of **14** shows two separate sets of singlets for the methyl groups at 2.22 and 1.71 ppm for the 'rac-like' isomer and at 2.14 and 2.05 ppm for the 'meso-like' isomer.
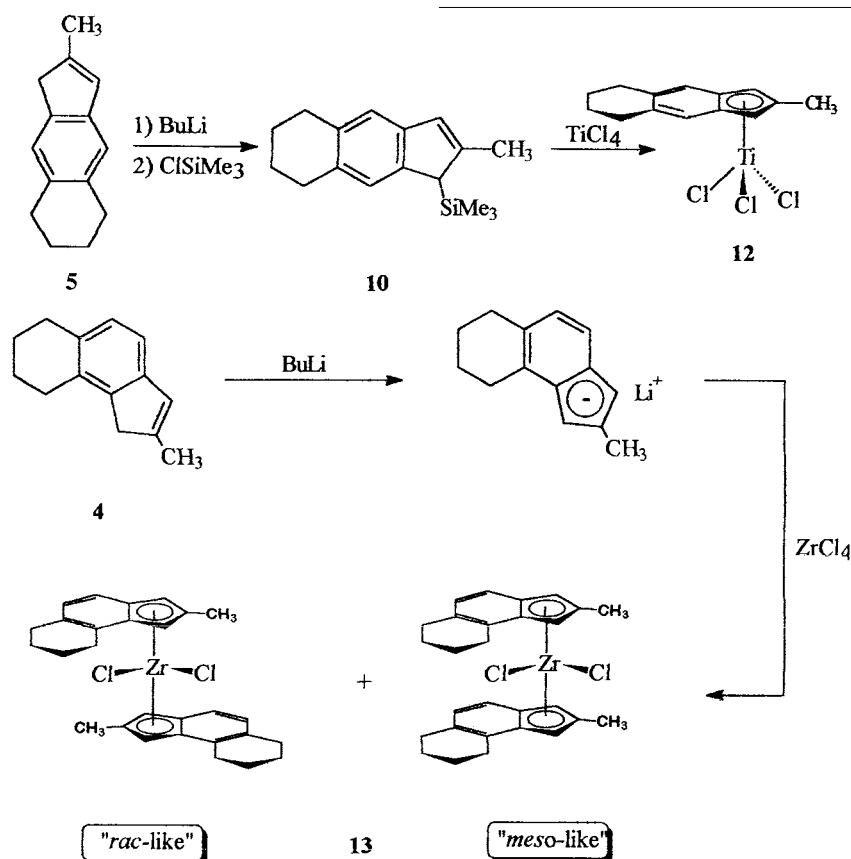
Table 1
Polymerization of propylene with precursors **13**–**16** activated with trityl/TIBA[a]

Compound	Cocatalyst	T_p (°C)	Yield (g)	10^{-6} A[b]	T_m (°C)	$(mmmm\%)$[c]
13	Trityl/TIBA	0	0.78	0.71	a-PP	a-PP
13	Trityl/TIBA	−20	0.96	0.70	a-PP	a-PP
14	Trityl/TIBA	0	1.64	1.50	108.4	49.0
14	Trityl/TIBA	−20	1.96	1.40	120.4	51.1
15	Trityl/TIBA	0	0.85	0.77	a-PP	a-PP
15	Trityl/TIBA	−20	3.75	2.30	a-PP	a-PP
16	Trityl/TIBA	0	0.13	0.12	70.6	40.4
16	Trityl/TIBA	−20	0.19	0.13	86.1	43.3

[a] Conditions: [Zr], 50 μM; Al/Zr, 20:1; [Zr]/trityl, 1:1; 15 psi of C_3H_6; t_p, 30 min for C_3H_6.
[b] Activity, g of polymer/(mol Zr[C_3H_6] × h).
[c] Determined by ^{13}C-NMR.

6 → **14**
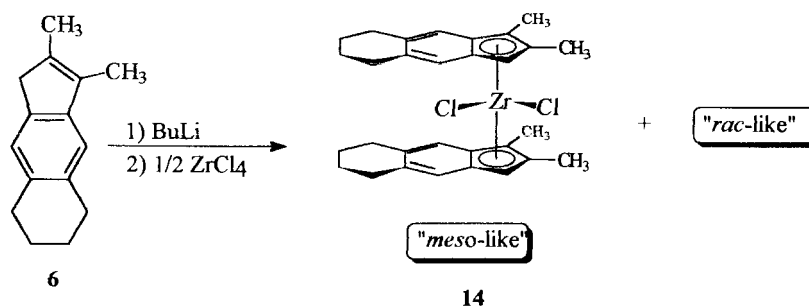
From the ^{1}H-NMR spectra, compound **15** appears to exist as a single 'meso-like' isomer since the two methyl groups appear as singlets at 2.28 and 2.23 ppm with no upfield shifted methyl groups as appears in compound **14**.

^{1}H-NMR spectrum of **16** shows a singlet for a methyl group at 1.98 ppm which is shifted further upfield than would be expected for a 'meso-like' isomer. The ^{1}H-NMR spectrum also confirms the presence of 2/3 of a

7 → **15**
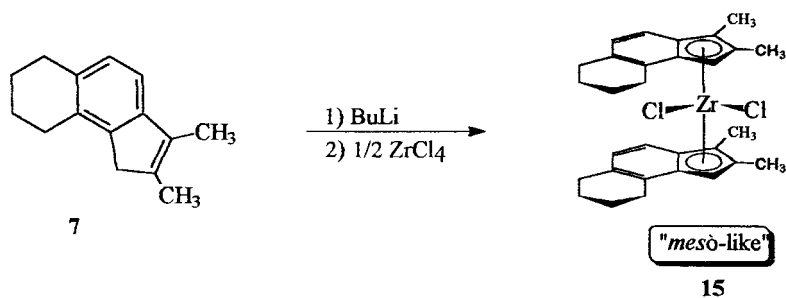
In addition to compounds **14** and **15**, a phenyl substituted derivative (**16**) was also synthesized by the procedure described for compound **13**. Compound **16** was isolated as a single 'rac-like' isomer in 52% yield. The

mole of toluene present in the crystalline product, consistent with microanalytical data for **16**. Attempts to remove the solvated toluene molecule by evaporation and gentle heating of **16** under vacuum were unsuccessful.
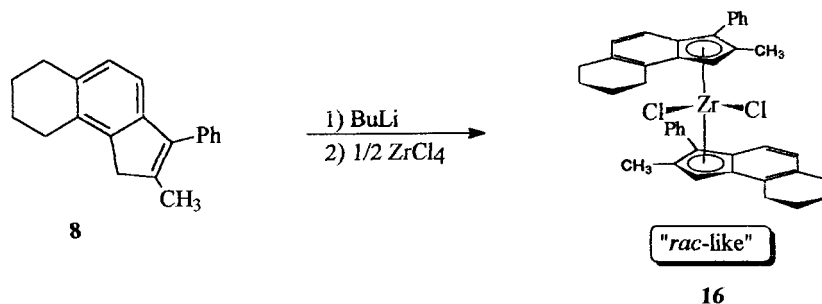

8 → **16**

Table 2
Polymerization of ethylene with precursors **13–16** activated with trityl/TIBA[a]

Compound	Monomer	Cocatalyst	T_p (°C)	Yield (g)	10^{-6} A[b]	T_m (°C)
13	C_2H_4	Trityl/TIBA	20	0.76	51.0	133.8
14	C_2H_4	Trityl/TIBA	20	1.20	80.0	134.2
15	C_2H_4	Trityl/TIBA	20	1.08	72.0	134.9
16	C_2H_4	Trityl/TIBA	20	0.30	2.00	135.4

[a] Conditions: [Zr], 50 μM; Al/Zr, 20:1; [Zr]/trityl, 1:1; 15 psi of C_2H_4; t_p, 1 min for C_2H_4.
[b] Activity, g of polymer/(mol of $Zr \times [C_2H_4] \times h$).

3.3. Polymerization results using unbridged tetrahydro-2-methylbenz[e]indenyl catalysts

The new catalyst precursors **11** and **12** were activated with MAO and used to polymerize styrene. The activities of the catalyst systems **11**/MAO and **12**/MAO were comparable [11] to that of other alkyl substituted indenyltitanium trichloride catalysts (ca. 2.0×10^7 g of PS/(mol of Ti·mol of styrene·h)] while the syndiotacticity of the PS was also greater than 92% for all polymerization conditions.

The catalyst precursor bis(η^5-tetrahydro-2-methyl-benz[e]indenyl)zirconium dichloride (**13**) (1:1 mixture of isomers) was activated with both MAO and trityl, and used to polymerize ethylene and propylene. For all polymerization conditions studied, the catalyst system **13**/trityl produced polypropylene with higher activity and molecular weight than that of the **13**/MAO system. Therefore, a comparison of the four new catalyst precursors was made using trityl as the cocatalyst. Table 1 shows a comparison of the propylene polymerization behavior of **13–16** when activated with trityl.

The precursors **13–16** activated with trityl were also highly active for the polymerization of ethylene, as shown in Table 2. The ethylene polymerization results show that catalysts **13-16**/trityl exhibit high activity greater than 5.0×10^7 g of polymer/(mol of $Zr \cdot [C_2H_4] \cdot h$). However, the catalyst system **16**/trityl has less than one tenth the activity of **13**/trityl. This reduction in activity is probably due to the addition of the bulky phenyl substituent present in the C-3 position, which decreases the ability of the monomer to coordinate to the metal center. In addition, the melting point of the polyethylene increases as the size of the substituent is increased. This result can be attributed to influence of the phenyl substituent, which decreases the amount of β-hydride elimination, resulting in higher molecular weight polymer.

The propylene polymerization catalysts **13–16**/trityl exhibit some remarkable properties. The purpose of introducing the tetrahydro substituent was to further hinder rotation of the pentahapto ligands as compared to the 2-methylbenz[e]indenyl systems. However, as

observed with the 2-methylbenz[e]indenyl catalyst, the catalyst system **13**/trityl produces only *a*-PP. As expected, the catalyst **13**/trityl is lower in activity than the 2-methylbenz[e]indenyl catalyst system due to the increased steric bulk introduced by the tetrahydro substituent.

For the case of the 2,3-dimethyl substituted catalyst system **14**/trityl, the mixture of '*rac*-like' and '*meso*-like' isomers produced polypropylene which was a blend of *a*-PP and *i*-PP. The blend was separated by extraction with diethyl ether to give a 25% insoluble *i*-PP fraction and a 75% soluble fraction. The insoluble fraction showed 51.1% *mmmm* pentads by ^{13}C-NMR and had a melting point of 120.4°C.

When the indene **7** was used to synthesize the catalyst precursor **15**, only one isomer was obtained. In addition to ^{1}H-NMR spectral evidence, the fact that only *a*-PP was produced by **15**/trityl with no crystalline domains is consistent with a '*meso*-like' structure of the catalyst precursor. However, the catalyst system **15**/trityl does exhibit high activity for propylene, producing 2.3×10^6 g of polymer/(mol of $Zr \cdot [C_2H_4] \cdot h$).

Finally, the catalyst **16**/trityl also shows some interesting characteristics. Although the steric bulk introduced by the phenyl substituent lowers the activity of the system **16**/trityl as compared to catalysts **13–15**/trityl, the catalyst system **16**/MAO produces crystalline polypropylene at -20°C. The ^{13}C-NMR spectrum of the polypropylene produced at -20°C indicates the presence of 43.3% *mmmm* pentads. In addition, the melting point of the polymer is fairly low (86.1°C) probably due to the low molecular weight of the polymer.

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[1] This work is taken from the Doctoral Dissertation of Patrick Foster, February 1997.

[2] While this manuscript was being prepared an article was published in which the silicon bridged zirconium metallocene complex of compound **4** was synthesized. N. Schneider, M.E. Huttenloch, U. Stehling, R. Kirsten, F. Schaper, H.H. Brintzinger, Organometallics 16 (1997) 3413.

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