

Synthesis and Catalyzing Behavior of Olefin Polymerization of *cis*-Cyclopentene Bridged Titanocenes

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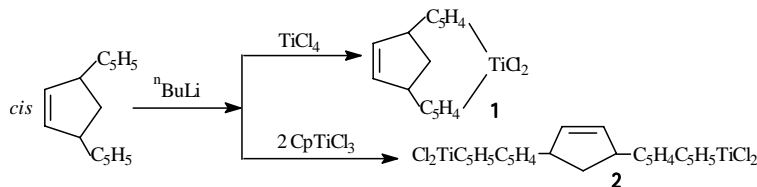
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Abstract: Two *cis*-cyclopentene bridged titanocenes have been synthesized. Two homogeneous Ziegler catalysts prepared by activation of synthesized compounds with methylalumoxane are active for ethylene polymerization reactions.

Keywords: Ansa-metalloenes, titanocene, ethylene polymerization.

The homogeneous Group 4 metallocene Ziegler catalysts are receiving an ever increasing attention lately. Their performance as selective α -olefin polymerization catalysts depends very critically on the structure of bent metallocene framework¹. Some efforts have been made to further improve the original Brintzinger ansa-metalloenes, the ethylene-bis (indenyl)- and -bis (tetrahydroindenyl) MX₂ systems², by making them conformationally still more rigid. Therefore we synthesized two *cis*-cyclopentene bridged titanocenes and investigated their performance of olefin polymerization.

The ligand, *cis*-3, 5-bis(cyclopentadienyl)cyclopentene, was synthesized by treating *cis*-3, 5-dibromocyclopentene with a little over two molar equivalents of new distilled cyclopentadiene by phase transfer method³ (Bu₄NBr). Subsequent deprotonation was achieved by treatment with *n*-butyl lithium. The cyclopentene bridged biscyclopentadienyl lithium reagent was reacted with TiCl₄ in tetrahydrofuran to give red mononuclear titanocene (compound **1**), and with CpTiCl₃ to give red binuclear titanocene (compound **2**). The reactions have been carried out as following equations:



Compound **1**: C₁₅H₁₄TiCl₂, m.p. >200°C (decomp.), yield 32.8%. Analytical data: found : C: 57.44, H: 4.38; calc. : C: 57.55, H: 4.51. ¹H NMR (CDCl₃, ppm): 6.44-6.66 (Cp, 8H, m), 6.17-6.20 (=CH, 2H, m), 3.74 (=C-CH, 2H, d), 1.83-2.45 (CH₂, 2H, m). IR (KBr, cm⁻¹): 3103.3, 2935.9, 1478.6, 1426.4, 818.4, 740.2. MS (positive ions, relative

intensity): m/z 312 (M^+ , 35), 277 (M-Cl, 18), 242 (M-2Cl, 100).

Compound **2**: $C_{25}H_{24}Ti_2Cl_4$, m.p. $>160^\circ C$ (decomp.), yield 42.7%. Analytical data: found : C: 53.29, H: 3.96; calc. : C: 53.40, H: 4.30. 1H NMR ($CDCl_3$, ppm): 6.33-6.57 (Cp, 18H, m), 5.94 (=CH, 2H, s), 4.32 (=C-CH, 2H, m), 1.58-2.21 (CH_2 , 2H, m). IR (KBr, cm^{-1}): 3103.3, 2947.0, 1696.0, 1481.0, 1015.8, 821.2.

The two compounds were activated by treatment with a large excess of MAO (Al/M ratio: 2000). The polymerization reactions were carried out in dilute toluene solution under 1.05 bar of olefins. The results show that both catalysts have good activity for ethylene polymerization, and very low activity for propylene polymerization. For ethylene polymerization, mononuclear titanocene gives higher activity than binuclear titanocene. The important polymerization data for ethylene polymerization: compound **1**: polymerization activity $12.6 (10^5 \text{ g}\cdot\text{PE}/\text{mol}\cdot\text{Ti}\cdot\text{h})$, crystallinity 1.95, polymer m.p. $142^\circ C$, $M_w=331540$, $M_w/M_n=3.54$; compound **2**: polymerization activity $3.57 (10^5 \text{ g}\cdot\text{PE}/\text{mol}\cdot\text{Ti}\cdot\text{h})$, crystallinity 2.48, polymer m.p. $290^\circ C$ (decomp.).

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