

**Two-state propagation mechanism for
propylene polymerization catalyzed by *rac*-[anti-ethylidene(1-*eta*.5-
tetramethylcyclopentadienyl)(1-*eta*.5-indenyl)] dimethyltitanium**

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if B has the fac stereochemistry depicted in Scheme I.

A combination of kinetic data for the conversion of A to C with estimated values of $[B]/[A]$ has allowed estimation of the rate of methyl migration (k_2). An Arrhenius plot of the data in Table I over the range 5–35 °C yielded a good straight line (correlation coefficient 0.999) and gave activation parameters of $\Delta H^\ddagger = 63 \pm 2 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -59 \pm 9 \text{ J mol}^{-1} \text{ K}^{-1}$ for the crucial methyl migration (carbonylation) step of the catalytic cycle.¹⁷

These data show that oxidative addition of MeI to A proceeds normally to give a methyl-rhodium complex B. The large values obtained for k_2 show that the previous nonobservation of B is due primarily to the rapidity with which it reacts to give species C. High rates of alkyl migration have been reported for other rhodium systems,¹⁸ much faster than for other unactivated metals in nonpolar solvents.⁸ This is probably the major reason why rhodium is such a good carbonylation catalyst.

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Supplementary Material Available: Experimental details including a warning on the extreme toxicity of methyl iodide and the rhodium carbonyl complexes (2 pages). Ordering information is given on any current masthead page.

(17) The values for the overall reaction, $\text{A} + \text{MeI} \rightarrow \text{C}$, in neat MeI are $\Delta H^\ddagger = 50 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -142 \text{ J mol}^{-1} \text{ K}^{-1}$, giving a ΔG^\ddagger_{298} of 92 kJ mol^{-1} compared with a ΔG^\ddagger_{298} of 79 kJ mol^{-1} for the methyl migration $\text{B} \rightarrow \text{C}$.

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Two-State Propagation Mechanism for Propylene Polymerization Catalyzed by *rac*-[*anti*-Ethylidene(1- η^5 -tetramethylcyclopentadienyl)(1- η^5 -indenyl)]dimethyltitanium

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ansa-Metallocene compounds with local C_2 symmetry have been actively investigated as catalysts for the isospecific polymerization of propylene.²⁻⁴ Recently, we reported that the nonsymmetric *rac*-[ethylidene(1- η^5 -tetramethylcyclopentadienyl)(1- η^5 -indenyl)]dichlorotitanium/methylaluminoxane (**1**/MAO) catalyst⁵

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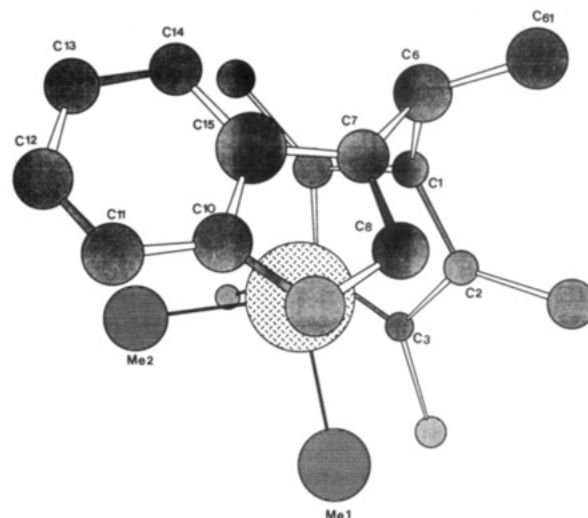


Figure 1. Molecular structure and atom-numbering scheme of *rac*-[ethylidene(1- η^5 -tetramethylcyclopentadienyl)(1- η^5 -indenyl)]dimethyltitanium (**2**). Important interatomic distances (Å) and bond angles (deg) are as follows: Ti–Me(1), 2.08 (1); Ti–Me(2), 2.00 (1); Ti–C(1), 2.21 (1); Ti–C(2), 2.32 (1); Ti–C(3), 2.44 (1); Ti–C(4), 2.47 (1); Ti–C(5), 2.37 (1); Ti–C(7), 2.10 (1); Ti–C(8), 2.17 (1); Ti–C(9), 2.41 (1); Ti–C(10), 2.56 (1); Ti–C(15), 2.40 (1); Ti–CEN(1), 2.07 (1); Ti–CEN(2), 2.01 (1); CEN(1)–Ti–CEN(2), 126.983; Me(1)–Ti–Me(2), 101.2 (5); CEN(1)–Ti–Me(1), 107.9 (4); CEN(2)–Ti–Me(1), 106.5 (3); CEN(1)–Ti–Me(2), 108.5 (4); CEN(2)–Ti–Me(2), 102.8 (3); C(1)–C(6)–C(7), 105.4 (9). [CEN(1) is centroid of C(1)–C(5); CEN(2) is centroid of C(7)–C(10) and C(15).]

produced stereoblock macromolecular chains comprising alternating sequences of stereoregular, crystallizable (*cry*) and stereoirregular, amorphous (*am*) polypropylene (PP),^{5,6} i.e., a thermoplastic elastomer (TPE-PP). We proposed that the catalytic species can exist in two interconverting states polymerizing propylene stereoselectively by one state, but nonselectively by the other state. We now report the synthesis, structure, and polymerization behavior of the title compound (**2**). The properties of **2** provide strong support for the proposed two-state propagation mechanism.

Compound **2** was synthesized by reacting a suspension of **1**⁷ in *n*-hexane with **2** equiv of methyl lithium. After filtration, concentration, and cooling at –20 °C, orange red crystals of **2** were obtained in 60% yield. Anal. Found (calcd): C, 77.2 (77.66); H, 8.18 (8.23). The ¹H NMR spectrum of **2**⁸ showed two singlets for the nonequivalent methyl groups bonded to titanium at –1.09 ppm and 0.17 ppm.

Crystals of **2** suitable for the X-ray diffraction study were grown by the slow cooling of a hexane solution of **2** at –20 °C. The space group was found to be $P2_1/c$, and the unit cell parameters are $a = 11.220$ (1) Å, $b = 9.366$ (2) Å, $c = 18.470$ (3) Å; $\beta = 106.75$ (1)°; and $D_{\text{calcd}} = 1.22 \text{ g cm}^{-3}$ for $Z = 4$. Least-squares refinement based on 729 observed reflections produced the final discrepancy indices $R = 0.054$ and $R_w = 0.056$.

The methyl group attached to the bridging carbon atom in **2** is oriented in an anti arrangement relative to the six-membered ring of the indenyl ligand (Figure 1). The two σ -bonded methyl substituents are located in sterically nonequivalent positions, with Me(2) oriented toward the six-membered ring of the indenyl ligand. Furthermore, the Ti–CH₃ distances are significantly different, with Ti–Me(1) = 2.08 (1) Å and Ti–Me(2) = 2.00 (1) Å.⁹

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(7) Reaction of [ethylidene(1- η^5 -tetramethylcyclopentadienyl)(1- η^5 -indenyl)]dilithium with $\text{TiCl}_4 \cdot 2\text{THF}$ gave **1** as the sole product. Under the same conditions, the reaction with TiCl_4 produced an equimolar mixture of **1** and its syn diastereomer.

(8) ¹H NMR spectrum (C_6D_6): –1.09 (s, 3 H), 0.17 (s, 3 H) for TiCH_3 ; 1.36 (s, 3 H), 1.50 (s, 3 H), 1.91 (s, 3 H), 1.95 (s, 3 H) for CH_3 of Cp^* ; 1.54 (d, 3 H) for ethylidene CH_2 ; 3.84 (q, 1 H) for ethylidene H; and 5.22 (d, 1 H), 6.88 (m), 7.68 (m), 7.20 (m) for the aromatic H of indenyl.

Table I. Kinetic Results of Propylene Polymerization

catalyst system	1/MAO			2/MAO		
T_p , °C	25	0	-20	25	0	-20
[C*], % of Ti	4.5	4.25	3.8	12.2	8.8	3.8
k_p , (M s) ⁻¹	210	240	360	150	270	1480
$k_{tr}^a \times 10^2$, s ⁻¹	1.5	0.9	0.40	0.38	0.79	1.52
$k_d^a \times 10^3$, s ⁻¹	5.7	4.4	3.8	3.34	2.6	
k_d^b (M s) ⁻¹						30

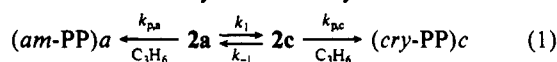
^a First-order rate constant. ^b Second-order rate constant.

Propylene was polymerized using Ti (27 μM) and MAO ([Al]/[Ti] = 2000) in toluene^{4,5} at three temperatures (T_p = -20, 0, 25 °C) and quenched at various times (t_p) with either normal or tritiated methanol. The PP was isolated, purified, and radioassayed.¹⁰ The kinetic results¹¹ (average of duplicate or triplicate) are summarized in Table I. An increase in T_p caused formation of more C*, but decreased both k_p and k_{tr}^A . The catalyst deactivation process is first order in [C*] above 0 °C but varies with [C*]² at -20 °C. The earlier results for the 1/MAO catalysts are included for comparison.

The PP produced at 25 °C exhibits excellent elastic properties: strength = 6.8 MPa, elongation to break = 850%, stress at 100% elongation = 3.0 MPa, and recovery after 100% elongation = 95%. The melting temperature for the *cry* domains, acting as physical cross-links at ambient temperature, is 62 °C. Their properties are very similar to those of the TPE-PP obtained with 1/MAO at the same T_p , the molecular structure of which has been determined.¹²

The stereochemistry of the polymers was determined by the analysis of 400-MHz C NMR.¹³ The [mmmm] contents were found to have decreasing values of 0.380, 0.300, and 0.229 with a decreasing T_p of 25, 0, and -20 °C, respectively. Detailed heptad analysis¹⁴ shows that the formation of stereoregular and stereoirregular sequences is consistent with the enantiomeric and Bernoullian models of stereochemical control,¹⁵ respectively.

In conclusion, the X-ray and NMR data demonstrate that complex **2** has nonequivalent Ti-Me groups, which provides a rationale for the assumption of a two-state propagation mechanism. Monomer insertion into the Ti-Me(2) (state **2c**; Me = PP chain) is stereoselective, whereas insertion into the Ti-Me(1) (state **2a**) results in stereoirregular enchainment. These processes and the interconversion of the catalytic states may be written as



For 0 °C < T_p ≤ 50 °C, many monomers are inserted with either

(9) The two Ti-CH₃ distances are both distinctly shorter than the Ti-CH₃ distance of 2.21 (2) Å found in (η⁵-C₅H₇)₂Ti(CH₃)₂; Atwood, J. L.; Hunter, W. E.; Hrnčir, D. C.; Samuel, E.; Alt, H.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 1757.

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(11) The specific ³H activity in PP was corrected for the kinetic isotope effect¹⁰ and converted to concentration of metal polymer bond [MPB], the value of which at zero yield (*Y*) by extrapolation gave [C*]. The rate of polymerization (R_p) was calculated from a *Y* versus t_p plot from which we calculated $k_p = R_p/[C^*][monomer]$. The value of k_{tr}^A was obtained¹⁰ by $([MPB]_t - [MPB]_0)k_p^0[monomer]/Y$. A plot of log R_p versus t_p afforded the first-order k_d , whereas a plot of $\Delta(R_p)^{-1}$ versus t_p gave the second-order k_d .

(12) For the TPE-PP obtained at $T_p = 25$ °C, from the measured equilibrium modules ($G_e = 0.56$ MPa), we estimated $a \sim 50$ using $G_e = 42\rho RT/a$, where ρ is the PP density. The percent crystallinity (X_c) and number average degree of polymerization (\overline{DP}_n) were determined to be 26% and 2300, respectively. These results gave $n = (\overline{DP}_n)(1 - X_c)/a \approx 34$ and $c = X_c(\overline{DP}_n)/n \approx 18$.

(13) ¹³C NMR spectra of PP were obtained by using *o*-dichlorobenzene solvent at 100 °C on a Varian XL-400 spectrometer operating at 100.6 MHz for carbon, 76° (14.5-ms) pulses, 0.75-s acquisition time, and TMS as internal reference.

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state before conversion to the other occurs. The values of k_{pa}/k_1 ($= a/[C_3H_6]$) and k_{pc}/k_{-1} ($= c/[C_3H_6]$) are large, and k_1^{-1} and k_{-1}^{-1} are much shorter than the kinetic chain lifetime. TPE-PP is thus produced possessing excellent mechanical and elastic properties. On the other hand, the PP obtained at $T_p \leq 0$ °C is without crystallinity because of two contributions. The lowering of T_p decreases the block lengths *a* and *c* as well as k_1/k_{-1} . Therefore, the nonstereoselective state is lower in energy than the stereoselective state.

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Supplementary Material Available: Detailed information on the crystal structure determination of **2** including atomic fractional coordinates and interatomic distances and angles (5 pages); listing of observed and calculated structure factors for **2** (5 pages). Ordering information is given on any current masthead page.

Isospecific Polymerization of Propylene Catalyzed by *rac*-Ethylenebis(indenyl)methylzirconium "Cation"

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The first homogeneous Ziegler-Natta catalyst Cp₂TiCl₂¹ (Cp = η⁵-cyclopentadienyl) activated with alkylaluminum chlorides exhibited low polymerization activity (*A*) for ethylene² and none for propylene. The use of methylaluminoxane³ (MAO) raised *A* by several orders of magnitude. Furthermore, metallocene/MAO systems,⁴ especially ones comprising chiral ansa-hapto ligands,⁵ can catalyze the isospecific polymerization of propylene. Recently, many "cationic" metallocene alkyls, usually with BPh₄ as the counterion, have been synthesized by reactions of alkyl derivatives of the metallocene with BPh₄ salts of R₃NH,^{6b-d,g} Ag,^{6a,7b} K,^{7b} and Cp₂Fe.^{7b,d} They were found to exhibit modest ethylene polymerization activity,⁶ but either they showed no ac-

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