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 results[11] (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 analysis[14] shows that the formation of stereoregular and stereoirregular sequences is consistent with the enantiomorphic 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

$$(am\text{-PP})a \xleftarrow[\mathrm{C_3H_6}]{k_{p,a}} \mathbf{2a} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathbf{2c} \xrightarrow[\mathrm{C_3H_6}]{k_{p,c}} (cry\text{-PP})c \qquad (1)$$

For 0 °C < T_p ≤ 50 °C, many monomers are inserted with either state before conversion to the other occurs. The values of $k_{p,a}/k_1$ (= $a/[\mathrm{C_3H_6}]$) and $k_{p,c}/k_{-1}$ (=$c/[\mathrm{C_3H_6}]$) 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 ≤ 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.

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(11) The specific ^{3}H activity in PP was corrected for the kinetic isotope effect[10] 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 $k_p = R_p/[\mathrm{C^*}][\mathrm{monomer}]$. The value of k_{tr}^A was obtained[10] by $([\mathrm{MPB}]_t - [\mathrm{MPB}]_0)k_p^{\circ}[\mathrm{monomer}]/Y$. 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_∞ = 0.56 MPa), we estimated $a \sim 50$ using $G_\infty = 42\rho RT/a$, where ρ is the PP density. The percent crystallinity (X_c) and number average degree of polymerization ($\overline{\mathrm{DP}}_n$) were determined to be 26% and 2300, respectively. These results gave $n = (\overline{\mathrm{DP}}_n)(1 - X_c)/a \approx 34$ and $c = X_c(\overline{\mathrm{DP}}_n)/n \approx 18$.

(13) ^{13}C 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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Isospecific Polymerization of Propylene Catalyzed by *rac*-Ethylenebis(indenyl)methylzirconium "Cation"

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The first homogeneous Ziegler–Natta catalyst Cp$_2$TiCl$_2$[1] (Cp = η^5-cyclopentadienyl) activated with alkylaluminum chlorides exhibited low polymerization activity (A) for ethylene[2] and none for propylene. The use of methylaluminoxane[3] (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 BPh$_4$ as the counterion, have been synthesized by reactions of alkyl derivatives of the metallocene with BPh$_4$ salts of R$_3$NH,[6b–d,g] Ag,[6a,7b] K,[7b] and Cp$_2$Fe.[7b,d] They were found to exhibit modest ethylene polymerization activity,[6] but either they showed no ac-

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Table I. Propylene Polymerizations[a]

run	catalyst		cocatalyst		T_p,	polymerization				T_m, °C		$[\eta]$,	M_w,[c]
no.	Zr	concn, μM	compd	concn, mM	°C	time, min	yield, g	A,[b] $\times 10^{-6}$	IY,[c] %	t-PP[d]	i-PP[d]	dL/g	$\times 10^{-4}$
1	**4**	75	**3**	0.075	20	30	8.80	8.5	36.9	128.8	141.4	0.32	2.4
2	**4**	75	**3**	0.075	0	30	9.45	6.7	88.4	142.4	147.2	0.66	5.9
3	4	75	**3**	0.075	−20	6	7.70	21	93.6	152.9	153.8	1.11	11
4	**4**	100	**3**	0.100	−55	6	6.81	(>10)[f]	96.3	161.1	160.8	1.45	16
5	**2**	125	MAO	312	20	30	2.39	1.4 1.3[5d]	59.6 74.6[5c]	134.8		0.31	2.4
6	**2**	125	MAO	312	0	30	0.21	0.09 0.15[5d]	76.0 74.4[5c]	141.5 143[5c]	 144[5c]	0.66 0.74[5c]	5.9 12[h,5c]
7	**2**	50	MAO	312	−20	60	0.08	0.033 0.031[5d]	75.0 75.3[5c]	146.8 147[5c]	 149[5c]	0.75 0.92[5c]	7.0 14.2
8	**2**	50	MAO	312	−55	60	0.01	0.0023[5d]	86.2[5d]	152[5d]	154[5d]		

[a] Toluene = 50 mL, $P(C_3H_6)$ = 1.68 Torr except in runs 4 and 8, where 50 mL of C_3H_6 was metered in. [b] In (g of PP)((mol of Zr)·$[C_3H_6]$·h)$^{-1}$. [c] Weight percent of PP insoluble in refluxing *n*-heptane. [d] t-PP is total polypropylene; i-PP is isotactic polypropylene. [e] log M_w = 1.25 × (log $[\eta]$ + 4) (Chiang, R. *J. Polym. Sci.* **1956**, *28*, 235). [f] Agitation limited. [g] M_w by GPC. [h] M_w by light scattering.

tivity for propylene polymerization or they gave low yields of atactic products.[6e,8] We report here that the title "cation" **1** is extremely active and stereoselective in propylene polymerization and that its catalytic activity and stereospecificity increase with a decrease of polymerization temperature (T_p).

All operations were performed using Schlenk tube techniques under an argon atmosphere. *rac*-Et(Ind)$_2$ZrCl$_2$[9] (**2**), LiB(C$_6$F$_5$)$_4$,[10] and MAO[11] were prepared according to published procedures. Triphenylcarbenium tetrakis(pentafluorophenyl)borate (**3**) was prepared by mixing LiB(C$_6$F$_5$)$_4$ (3.00 g, 4.25 mmol) and triphenylmethyl chloride (1.42 g, 5.09 mmol) in 200 mL of dry *n*-hexane and refluxing overnight. The yellow solid was dissolved in CH$_2$Cl$_2$ and the LiCl removed by filtration. Recrystallization of the product from CH$_2$Cl$_2$/hexane afforded orange crystals of **3** (2.51 g, 2.72 mmol, 64% yield): ^{1}H NMR (C$_6$D$_6$) δ 8.27 (t, J = 7.5 Hz, 3 H), 7.88 (t, J = 7.9 Hz, 6 H), 7.68 (t, J = 8.5 Hz, 6 H). Anal. Found (calcd): C, 55.80 (55.99); H, 1.69 (1.64). *rac*-Et(Ind)$_2$Zr(CH$_3$)$_2$ (**4**) was obtained by the reaction of **2** (0.20 g, 0.48 mmol) in 100 mL of dry toluene with methyllithium (0.68 mL of a 1.4 M solution) between 0 and 25 °C. Filtration, concentration, and cooling at −20 °C yielded 0.064 g of **4** (25%): ^{1}H NMR (C$_6$D$_6$) δ −0.96 (s, 6 H, CH$_3$), 2.60–2.85 (m, 4 H, C$_2$H$_4$), 5.65 [d, J = 3.3 Hz, 2 H, CH(C$_5$)], 6.42 [d, J = 3.3 Hz, 2 H, CH(C$_5$)], 6.85–7.40 (m, 8 H, Ar).

In analogy to the other metallocene "cation" producing reactions,[6,7] **1** was formed by the reaction of **4** with **3** (eq 1). The proton NMR spectrum of **5** was readily observed.

$$\underset{\mathbf{4}}{\mathrm{Et(Ind)_2Zr(CH_3)_2}} + \underset{\mathbf{3}}{\mathrm{Ph_3C^+B(C_6F_5)_4^-}} \rightarrow \underset{\mathbf{1}}{\mathrm{[Et(Ind)_2Zr(CH_3)]^+B(C_6F_5)_4^-}} + \underset{\mathbf{5}}{\mathrm{Ph_3CCH_3}} \qquad (1)$$

Polymerizations of propylene, at T_p ranging from −55° to 20 °C, were carried out in a 250-mL crown-capped glass pressure reactor containing 50 mL of toluene and were equilibrated with propylene at 1.7 Torr. Equimolar amounts of **4** and **3** were introduced in that order to form **1** in situ. Polymerization began immediately, reaching a maximum rate (R_p) within 2–3 min. There was little or no decay of R_p as monitored by pressure drop. The polymerization was quenched with methanol, and the polymer was worked up as detailed elsewhere.[5c,d,11] The values of A were calculated using the measured solubility of propylene.[5c] There are two measures for stereospecificity in propylene polymerization: the percent yield of refluxing *n*-heptane insoluble i-PP (IY) and the isotacticity of the PP as judged by T_m (melting temperature), crystallinity, homosteric sequence distribution, etc.

The polymerization activity of **1** is very high; it is 6 times greater than the activity of the **2**/MAO system at 20 °C (compare runs 1 and 5, Table I). IY, T_m, and M_w were all similarly low for PP produced by both catalysts at this T_p. Unexpectedly, **1** has an A which is *greater at lower temperatures*; at $T_p \leq -20$ °C the polymerizations were agitation limited after only a few minutes.[12] Furthermore, the stereospecificity, as judged by IY, T_m, and M_w, also became greater at low T_p. At −55 °C, **1** produced 96.3% i-PP with $T_m \sim 160$ °C, indicating very high stereoregularity. The latter was supported by ^{13}C NMR steric sequence distributions (to be published).

MAO was found to be detrimental to propylene polymerizations catalyzed by **1**. In separate runs using 3.75 μmol of **4** + **3**, the addition of 0.5 mmol of MAO at t_p of 1 min, 6 min, and 15 min produced 1.45, 4.53, and 7.02 g of PP, respectively, with corresponding A values of 1.03 × 10^6, 3.22 × 10^6 and 5 × 10^6 (g of PP)((mol of Zr)·[monomer]·h)$^{-1}$. The yields and A are 9.45 g and 6.7 × 10^6 in the absence of MAO. The addition of a mixture of **4**, **3**, and MAO to propylene in toluene produced only a small amount of polymer. ^{1}H, ^{13}C, and ^{19}F NMR showed that **4** reacts with trimethylaluminum, which is an unavoidable contaminant in MAO (to be published).

The A of **2**/MAO catalyst decreased with temperature with an Arrhenius dependence of 10 kcal/mol[5d] (runs 5–8 of Table I). This can be explained by the energies of activation required for both the extraction of chloride ion from **2** and methylation of the resulting cation by MAO.

Our work is complementary to an alternate synthesis of "cation-like" zirconocene methyl species described by Marks and co-workers.[8] Our stereorigid *ansa*-metallocene "cation" exhibits high activity and stereospecificity for propylene polymerization, whereas their nonstereorigid system has low activity and is nonspecific.

Registry No. 2, 100080-82-8; **3**, 136040-19-2; **4**, 49596-04-5; LiB(C$_6$H$_5$)$_4$, 2797-28-6; CH$_2$=CHCH$_3$, 9003-07-0; CH$_2$=CHCH$_3$ (isotactic homopolymer), 25085-53-4; LiMe, 917-54-4; (Ph)$_3$CCl, 76-83-5.

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