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Transition-Metal Organometallic Compounds as Cocatalysts in Olefin Polymerization with $MgCl_2$-Supported Catalysts

Maurizio Galimberti,* Fabrizio Piemontesi, Umberto Giannini, and Enrico Albizzati

Himont Italia S.r.l., Research Centre G. Natta, P.le G. Donegani 12, I-44100 Ferrara, Italy

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ABSTRACT: Zirconium tetrabenzyl was used as the cocatalyst in olefin polymerization together with $MgCl_2$-supported titanium catalysts. Its behavior was compared with those of aluminum and titanium organometallic compounds. In propylene polymerization performed with a $MgCl_2/TiCl_4$ catalyst containing ethyl benzoate as the internal donor and with tetrabenzylzirconium as the cocatalyst, a polypropylene with 93 as its isotactic index was obtained, without the need of any external donor. We present a tentative explanation, based on the study of the interactions between the different components of the catalytic system.

Introduction

The replacement of aluminum alkyls, as cocatalysts in Ziegler–Natta catalysis, with transition-metal organometallic compounds, was studied for the first time in the 1950s by Natta and co-workers and later by other authors, in ethylene and propylene polymerization.[1]

These studies were carried out to demonstrate that the growth of the polymer chain takes place by insertion of the monomer into a transition metal–carbon bond and not into the Al–C bond.

The propylene polymerization with $TiCl_3$ and either aluminum tribenzyl or titanium tetrabenzyl as cocatalysts[2] showed that the two catalyst systems exhibit similar activity and stereospecificity. This confirmed that the main role played by the cocatalyst is the alkylation of the transition-metal salt, besides its activity as effective scavengers of impurities in polymerization media.

More recently, bis(cyclopentadienyl)titanium dimethyl (Cp_2TiMe_2) was found to form with $TiCl_3$ a high isospecific catalyst for propylene polymerization.[3] The stereoregularity of such a polymer [isotacticity index (II) > 98] is much higher than that of the polymer prepared in the presence of AlR_3 as cocatalyst (II $\approx$ 70). An even more relevant difference in the behavior of the two cocatalysts was observed in the propylene polymerization promoted by catalysts based on $TiCl_4$ supported on $MgCl_2$. In the absence of Lewis bases, the catalyst isospecificity is drastically improved by using Cp_2TiMe_2 as cocatalyst in place of alkylaluminum compounds, but at the same time the catalytic activity strongly decreases. In order to justify the high stereospecificity of this catalyst system, the presence of bimetallic active centers containing the metallocene was hypothesized.[3c]

On these bases, we found it worthwhile to investigate the behavior of homoleptic benzyl derivatives of titanium and zirconium,[4] as cocatalysts in olefin polymerization. We have thus developed a new family of Ziegler–Natta catalysts, useful for olefin homo- and copolymerization, where titanium tetrabenzyl ($TiBz_4$) and zirconium tetrabenzyl ($ZrBz_4$) are used as cocatalysts in combination with $MgCl_2$-supported titanium catalysts.[5]

These benzyl derivatives have been used so far as catalysts, either without cocatalysts, in solution, or supported on a carrier[6] or in the presence of water,[7a] aluminum or transition-metal alkyls or halides,[7b] methylaluminoxane,[8a,b] or perfluorinated arylboron compound[8c–e] for ethylene, propylene, and styrene polymerization.

In this work we investigated the behavior in ethylene and propylene polymerizations of $ZrBz_4$ used as cocatalyst in combination with $MgCl_2$-supported Ti catalysts. We compared its performances with those of $TiBz_4$, aluminum triisobutyl (Ali-Bu_3), and Cp_2TiMe_2 and studied the properties of the polymer obtained therefrom.

Results and Discussion

Ethylene Polymerization. The results obtained in ethylene polymerization with different $MgCl_2$-supported catalysts and with cocatalysts based on aluminum and transition-metal organometallic compounds are reported in Table I.

As observed for Ali-Bu_3, the polymerization activity with $ZrBr_4$ strongly depends on the solid catalyst employed, thus suggesting that the active centers are located on the solid catalyst. $ZrBz_4$ used in the absence of any $MgCl_2$-supported titanium catalyst affords indeed a much lower activity in the ethylene polymerization carried out under the same experimental conditions.

The order of activity of the cocatalysts employed with catalyst C appears to be Ali-Bu_3 > $ZrBz_4$ > $TiBz_4$ > Cp_2TiMe_2 ≥ $AlBz_3$ > Cp_2ZrMe_2, and it is confirmed by the results obtained with catalysts A and B.

The lower activity obtained with $ZrBz_4$ instead of Ali-Bu_3 could be justified by assuming a lower alkylating capability of the zirconium organometallic compound with respect to Ali-Bu_3.

Polyethylenes obtained with those different catalyst systems have very similar melting points. This suggests that also polyethylenes from cocatalysts other than Ali-Bu_3 have a linear structure, as already reported by Soga for Cp_2TiMe_2.[9]

Polyethylenes obtained with $ZrBz_4$ as cocatalyst show higher molecular weight than those from the other cocatalysts.[10] A possible explanation for the decreasing of termination reactions is the absence of a chain-transfer agent like the aluminum alkyl.

Furthermore, by polymerizing in the presence of hydrogen, the intrinsic viscosity is more than twice that of polyethylenes obtained by using Ali-Bu_3 or Cp_2TiMe_2 as cocatalysts. This result could partially be ascribed to a decrease of hydrogen concentration during the polymerization due to the hydrogenation of ethylene by the catalyst system containing $ZrBz_4$, as it appears from the data reported in Table II.

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Table I. Ethylene Polymerization with $MgCl_2/TiCl_4$ Catalysts and Organometallic Compounds of Al, Ti, and Zr as Cocatalysts

run	catalyst type	catalyst Ti (% wt)	catalyst mg	cocatalyst type	cocat/Ti (mol/mol)	activity (g_{PE}/g_{Ti}·h)	η_{inh} (dL/g)	mp (°C)
1	A[a]	2.85	32.4	Ali-Bu_3	30	3900	11.3	134.3
2			29.8	$ZrBz_4$	30	500	ins[e]	133.3
3			32.3	Cp_2TiMe_2	30	10	nd	nd
4	B[a]	1.70	63.8	Ali-Bu_3	25	950	11.4	135.0
5			61.4	$ZrBz_4$	25	190	ins[e]	135.5
6			63.2	Cp_2TiMe_2	25	30	nd	133.9
7	C[b]	8.25	10.0	Ali-Bu_3	50	337000	2.5	nd
8			12.0	$AlBz_3$	90	33000	4.1	nd
9			17.0	$TiBz_4$	25	67000	3.9	nd
10			10.0	$ZrBz_4$	50	167000	5.7	nd
11			21.0	Cp_2TiMe_2	35	45000	3.2	nd
12			16.0	Cp_2ZrMe_2	55	150	nd	nd
13	$ZrBz_4$[c]		264.4	none		2[d]	nd	nd

[a] Polymerization conditions: *n*-heptane, [M] cocatalyst = 2 mmol/L, $P_{C_2H_4}$ = 0.12 MPa, T = 70 °C, t = 1 h. [b] Polymerization conditions: *n*-heptane = 1000 mL, $P_{C_2H_4}$ = 1.01 MPa, P_{H_2} = 0.5 MPa, T = 70 °C, t = 3 h (except for runs 7 and 8, t = 1 h). [c] [$ZrBz_4$] = 2 mmol/L, $P_{C_2H_4}$ = 0.12 MPa, T = 70 °C, t = 1 h. [d] g_{PE}/g_{Zr}·h. [e] The values obtained (>20) were regarded as not reliable (see ref 10).

Table II. Ethylene Hydrogenation during Polymerization with $MgCl_2/TiCl_4$ Catalysts and $ZrBz_4$ as Cocatalyst[a]

run	catalyst type	catalyst Ti (wt %)	catalyst mg	Zr/Ti (mol/mol)	time (h)	C_2H_4 (MPa)	H_2 (MPa)	activity (g_{PE}/g_{Ti})	final molar % C_2H_4	final molar % C_2H_6
14	D	8.0	10	52	1	1.01	0.5	137 000	95	5
15	E	9.0	21	25	2	1.51	0.5	159 000	88	12

[a] Polymerization conditions: *n*-heptane = 430 mL for run 14 and 200 mL for run 15, T = 70 °C.

Table III. Propylene Polymerization with $MgCl_2/TiCl_4$ Catalyst and Organometallic Compounds of Al, Ti, and Zr as Cocatalysts[a]

run	catalyst type	catalyst Ti (wt %)	catalyst mg	cocatalyst type	cocat/Ti (mol/mol)	activity (g_{PP}/g_{Ti}·h)	II	$M_w \times 10^{-5}$	M_w/M_n	mmmm	mmmr	rmmr	mmrr	xmrx	mrmr	rrrr	rrrm	mrrm
										steric pentad composition (%)								
16	B	1.7	55.3	Ali-Bu_3	17	8480	26	1.9	7.0	47.8	10.8	2.2	10.7	8.8	2.8	5.8	5.4	5.7
17			57.9	$ZrBz_4$	17	570	38	3.8	8.1	57.2	8.4	1.7	8.8	7.0	1.5	6.2	5.1	4.1
18			54.3	Cp_2TiMe_2	17	15	95	1.8	3.8	95.0	3.1		1.9					

[a] Polymerization conditions: 240 mL of *n*-heptane, P = 0.12 MPa, T = 60 °C, t = 1 h.

Table IV. Propylene Polymerization with $MgCl_2/TiCl_4$/Ethyl Benzoate Catalyst and Organometallic Compounds of Al, Ti, and Zr as Cocatalysts[a]

run	catalyst type	catalyst Ti (% wt)	catalyst mg	cocatalyst type	cocatalyst mmol/L	cocat/Ti (mol/mol)	activity (g_{PP}/g_{Ti}·h)	II	η_{inh} (dL/g)	M_w/M_n	mp (°C)	ΔH (J/g)
19	F	2.0	53.7	Ali-Bu_3	1.4	17	7310	72	1.5	6.0	153.7	62.1
20			50.9	$ZrBz_4$	1.4	17	3120	93	2.0	4.4	157.6	91.2
21			174.2	Ali-Bu_3	10.0	17	7950	45	1.0	10.5	155.5	33.5
22			171.4	$AlBz_3$	10.0	17	3500	47	1.9	nd	156.6	38.7
23			172.4	$ZrBz_4$	10.0	17	3490	90	2.5	7.0	156.1	61.4
24			53.3	Ali-Bu_3/PEA[b]	1.4	16	3900	98	3.0	3.9	160.0	91.2
25			28.1	$ZrBz_4$/PEA[c]	1.6	16	27	nd	nd	nd	nd	nd

[a] Polymerization conditions: *n*-heptane, P = 0.12 MPa, T = 60 °C, t = 1 h, catalyst EB = 8.3% wt. [b] PEA = *p*-ethyl anisate, Al/PEA = 3 mol/mol. [c] Zr/PEA = 3 mol/mol.

Propylene Polymerization. The polymerization of propylene was studied with $MgCl_2/TiCl_4$ and $MgCl_2/TiCl_4$/ethyl benzoate (EB) as catalysts and with the organometallic compounds of aluminum, titanium, and zirconium reported in Tables III and IV as cocatalysts.

In the absence of a Lewis base as internal donor[11] the polymerization activity strongly depends on the nature of the cocatalyst, following the order already observed for ethylene polymerization: Ali-Bu_3 > $ZrBz_4$ > Cp_2TiMe_2. $ZrBz_4$ is completely inactive as a single-component catalyst, under the same polymerization conditions.

As for polyethylene, the highest molecular weights were obtained with $ZrBz_4$ as cocatalyst. As far as the other molecular properties, i.e., molecular weight distribution (MWD) and stereoregularity, are concerned, only slight differences were observed between polypropylenes obtained with Ali-Bu_3 or $ZrBz_4$ as cocatalysts. Particularly, the steric pentad composition appears to be similar and indicates the low stereospecificity of both catalyst systems.

The results obtained with Cp_2TiMe_2 as cocatalyst were in agreement with what was discovered and reported by Soga. The polypropylene was highly stereoregular and the MWD considerably narrower.

Regioirregularities were not observed in any of the polypropylenes, even in the more stereoirregular fractions.

On the basis of these results, the behavior of $ZrBz_4$ and Ali-Bu_3, used as cocatalysts in combination with $MgCl_2$-supported titanium catalysts without any electron donors, appears to be very similar, the only significant difference being the catalytic activity. In other words, both the cocatalysts are able to activate aspecific and isospecific catalytic centers.

Remarkable differences were, on the other hand, observed in the propylene polymerization carried out in the presence of $MgCl_2$-supported titanium catalyst containing EB as the internal donor (see Table IV).

As already reported, the stereospecificity of this catalyst with Ali-Bu_3 as cocatalyst is poor,[12] particularly at high

Table V. Steric Pentad Composition of Polypropylenes Obtained with $MgCl_2/TiCl_4$/EB Catalyst (Catalyst F) and Ali-Bu_3 or $ZrBz_4$ as Cocatalysts

	cocatalyst		steric pentad composition									
run	type	mmol/L	mmmm	mmmr	rmmr	mmrr	xmrx	mrmr	rrrr	rrrm	mrrm	II
19	Ali-Bu_3	1.4	80.0	6.2	0.8	5.2	2.7	0.8	1.5	1.4	2.5	72
21	Ali-Bu_3	10.0	66.1	7.9	1.1	7.7	5.2	1.4	3.2	3.3	4.1	45
20	$ZrBz_4$	1.4	85.0	4.6	0.6	3.6	1.5	0.4	1.4	1.1	1.7	93
23	$ZrBz_4$	10.0	83.0	4.0	0.6	3.3	1.3		2.7	2.0	3.1	90

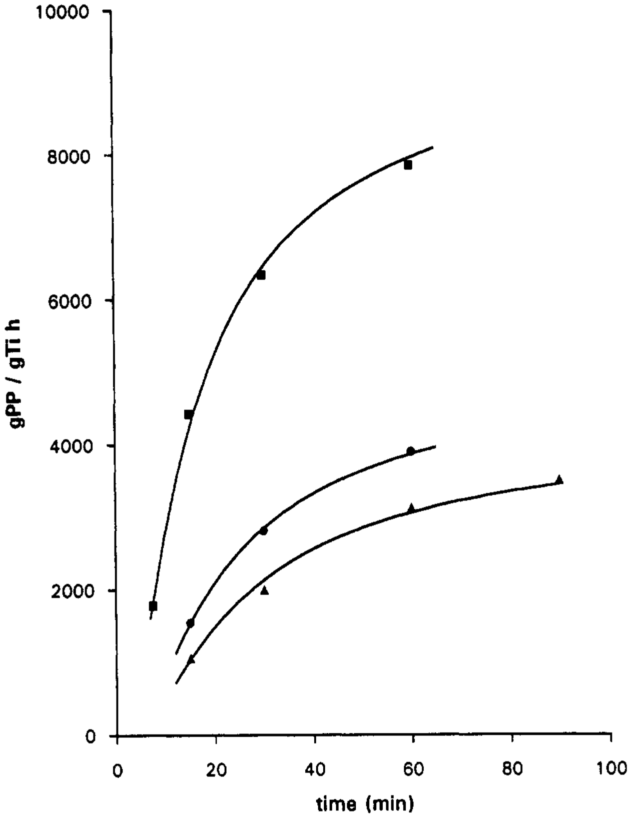

Figure 1. Polymerization activity versus polymerization time for propylene polymerization performed with $MgCl_2/TiCl_4$/ethyl benzoate catalyst (catalyst F) and $ZrBz_4$ (▲), Ali-Bu_3/*p*-ethyl anisate (●), or Ali-Bu_3 (■) as cocatalysts.

Table VI. Propylene Polymerization with $MgCl_2/TiCl_4$/Ethyl Benzoate Catalyst and Organometallic Compounds of Al and Zr as Cocatalysts[a]

	catalyst			cocatalyst			η_{inh}
run	type	Ti (% wt)	mg	type	*t* (min)	II	(dL/g)
26	F	2.0	54.2	Ali-Bu_3	7.5	71	1.6
19			50.5	Ali-Bu_3	60	72	1.5
27			56.4	$ZrBz_4$	15	94	2.3
28			54.2	$ZrBz_4$	90	94	2.3

[a] Polymerization conditions: *n*-heptane, $P = 0.12$ MPa, $T = 60$ °C, [M] cocatalyst = 1.4 mmol/L, catalyst EB = 8.3% wt.

Table VII. Reaction between Ethyl Benzoate and Ali-Bu_3 or $ZrBz_4$[a]

time	EB not reacted (%)[b]		time	EB not reacted (%)[b]	
(min)	Ali-Bu_3	$ZrBz_4$	(min)	Ali-Bu_3	$ZrBz_4$
0	100	100	10	35	8
1	67	58	15	34	0
5	35	31	60	31	0

[a] Reaction conditions: *n*-heptane, [EB] = 0.125 mmol/L, [Al]/[EB] = 12 mol/mol, [Zr]/[EB] = 12 mol/mol, $T = 60$ °C. [b] Obtained by GC analysis.

metal alkyl concentration. As shown in Table V, the fully isotactic pentad content of the polymer decreases from about 80% to about 66%, as the aluminum alkyl concentration increases from 1 to 10 mmol/L.

The low stereospecificity of this catalyst system was ascribed by most authors to coordination and secondary reactions of aluminum trialkyl with EB.[13] This gives rise to the displacement of the stereoregulating Lewis base from the catalyst surface. It is well-known that, to reach a high stereospecificity, this must be prevented by adding further Lewis base as external donor, together with the cocatalyst.[11]

On the other hand, the catalyst system containing $ZrBz_4$ as cocatalyst is able to give stereoregular polypropylene, even without an external donor. The concentration of $ZrBz_4$ does not affect the stereospecificity of the catalyst system (see Tables IV and V). The activity and the stereospecificity are comparable to those of the system containing Ali-Bu_3 and *p*-ethyl anisate (PEA) as the external donor. The time dependence of the polymerization activity, using Ali-Bu_3, Ali-Bu_3/PEA, and $ZrBz_4$ as cocatalysts, is reported in Figure 1.

The isotacticity index and molecular weight of the polymers obtained with the different cocatalysts are not affected by the polymerization time, at least at low metal alkyl concentration (see Table VI).

The different behavior of Ali-Bu_3 and $ZrBz_4$ as cocatalysts does not depend on the nature of the organic radical bound to the metal, because $AlBz_3$ has almost the same activity as $ZrBz_4$, as previously observed in propylene polymerization with $TiCl_3$,[2] while the stereospecificity is much lower and similar to that obtained with Ali-Bu_3.

Furthermore, the different results obtained with aluminum and zirconium alkyl cocatalysts cannot be ascribed to a lower reactivity of $ZrBz_4$, with respect to Ali-Bu_3, toward the organic ester. As a matter of fact, $ZrBz_4$ reacts with EB in hydrocarbon solution faster than Ali-Bu_3, giving benzylphenyl ketone and dibenzylphenylcarbinol as the main reaction products. The higher reactivity of $ZrBz_4$ was verified both by GC–mass spectroscopy analysis (see Table VII) and by following the reaction with proton NMR (see Figures 2 and 3).

The extremely low polymerization activity obtained with $ZrBz_4$ and PEA as the cocatalyst system (see Table IV) can thus be explained by taking into account the strong interaction between the organometallic compound and the organic ester.

The situation appears to be different when the organometallic compounds react with the organic ester present on the solid catalyst.

By reacting the $MgCl_2/TiCl_4$/EB catalyst with Ali-Bu_3 or $ZrBz_4$ under conditions similar to those adopted in polymerization tests (1–2 mmol/L as the aluminum alkyl concentration), a comparable amount of unreacted EB was found on the catalyst after filtration and washing with *n*-heptane (see Table VIII, runs 1 and 2). By increasing the metal alkyl concentration, the amount of unreacted EB considerably decreased, more when the catalyst was reacted with Ali-Bu_3.

As reported above, the stereospecificity of the catalyst system containing Ali-Bu_3 was considerably affected by the increase of the cocatalyst concentration, while that of the system based on $ZrBz_4$ remained almost the same.

Therefore, the different isospecificity of the catalyst containing EB, used with Ali-Bu_3 or $ZrBz_4$ as cocatalyst,

Table VIII. Reaction between $MgCl_2/TiCl_4$/Ethyl Benzoate Catalyst and Ali-Bu_3 or $ZrBz_4$[a]

	catalyst		cocatalyst		cocatalyst/Ti	cocatalyst/EB		catalyst after reaction	
run	type	mg	type	mmol/L	(mol/mol)	(mol/mol)	time (min)	% EB[b]	cocat/Mg (mol/mol)
29	F	295	Ali-Bu_3	1.5	17.5	12.5	60	50.0	1:12
30		251	$ZrBz_4$	1.5	17.5	12.5	60	54.0	1:8
31		992	Ali-Bu_3	27.6	18.5	12.6	15	49.4	nd
32		996	Ali-Bu_3	27.6	18.4	12.5	30	32.6	nd
33		990	Ali-Bu_3	27.6	16.7	12.6	60	26.5	nd
34		502	$ZrBz_4$	27.0	18.0	12.3	15	50.6	nd
35		506	$ZrBz_4$	28.0	18.2	12.4	30	41.0	nd
36		502	$ZrBz_4$	27.0	18.1	12.3	60	37.3	nd

[a] Reaction conditions: *n*-heptane, $T = 60$ °C. [b] Ethyl benzoate on the catalyst after the reaction, with respect to the initial amount.

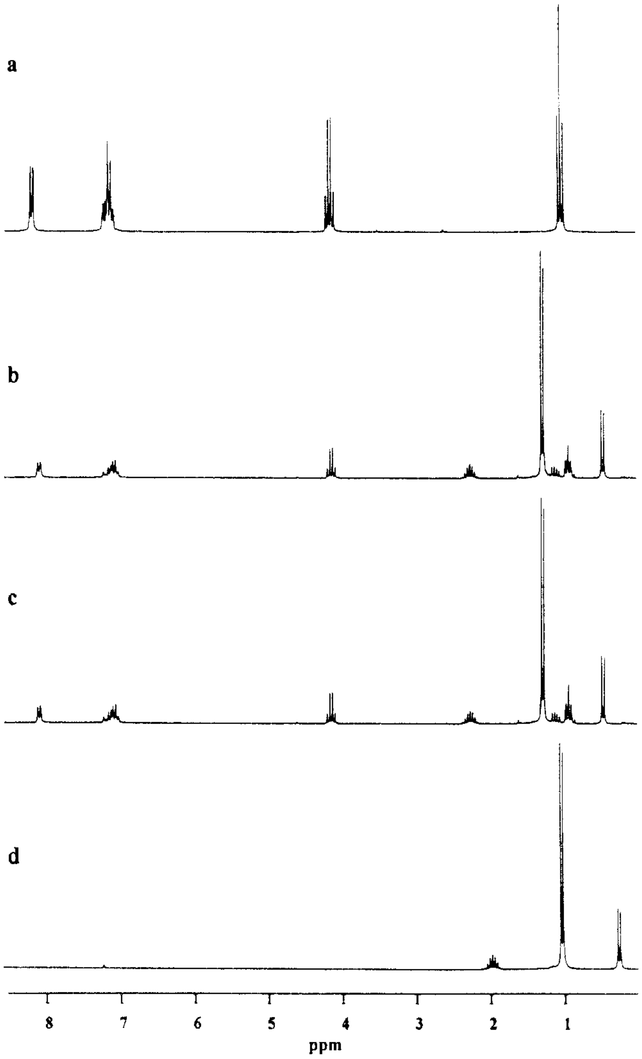

Figure 2. Reaction between ethyl benzoate and Ali-Bu_3 in the NMR tube. ^1H NMR of the organic ester (a), the cocatalyst (d), and the reaction products after 5 min (b) and 60 min (c).

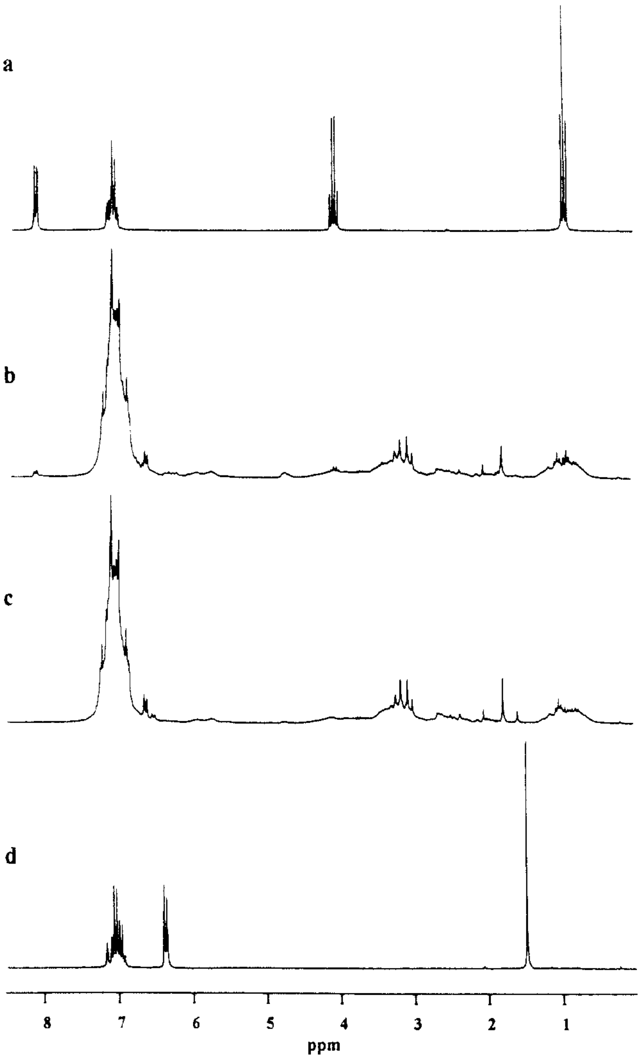

Figure 3. Reaction between ethyl benzoate and $ZrBz_4$ in the NMR tube. ^1H NMR of the organic ester (a), the cocatalyst (d), and the reaction products after 5 min (b) and 60 min (c).

cannot be ascribed to the actual organic ester amount present on the catalyst during the polymerization.

To rationalize the experimental findings, we suggest an explanation that takes into account the stereoregulating mechanism of the Lewis bases suggested by Corradini.[14]

According to this model, dimeric stereospecific titanium species are present on the (100) faces of $MgCl_2$ crystallites whereas the Lewis base saturates the vacancies of Mg atoms present on the (110) faces. This avoids the coordination of titanium species on these planes, which would lead to the formation of aspecific centers.

The reaction of Ali-Bu_3 with the catalyst partially displaces the Lewis base from the (110) faces and allows the migration and coordination of titanium halides on the coordinatively unsaturated Mg atoms which became available on these planes. As a consequence, aspecific centers are generated and the stereospecificity of the catalyst decreases.

We suggest that the reaction products of $ZrBz_4$ with EB remain bonded on the (110) faces, thus avoiding the formation of aspecific centers.

The results reported in Table VIII seem to support this hypothesis: after reaction with either $ZrBz_4$ of Ali-Bu_3 a larger amount of zirconium with respect to aluminum is present on the catalyst.

Experimental Section

All reactions involving air-sensitive compounds were carried out under a dry nitrogen atmosphere according to the Schlenk-tube technique.

Chemicals were purchased from Fluka and used as received unless stated otherwise. *n*-Heptane was purified by refluxing over Ali-Bu_3 and subsequent distillation under nitrogen.

$MgCl_2$/$TiCl_4$ Catalysts. Catalysts A and C–E were prepared by reaction of a spherical $MgCl_2{\cdot}nC_2H_5OH$ adduct with $TiCl_4$. Ti content (wt %): A, 2.85; C, 8.25; D, 8.0; E, 9.0. Surface area (m^2/g): A, 66; C, 376.

Catalyst B was prepared by comilling $MgCl_2$ and $TiCl_4$ for 1 h. Ti content (wt %) = 1.70; surface area (m^2/g) = 18.

Catalyst F was prepared as reported.[15] Ti content (wt %) = 2.0; EB content (wt %) = 8.3.

Cocatalysts. $TiBz_4$ was synthesized according to the literature.[4]

$ZrBz_4$ was synthesized by modifying the method reported in the literature.[4] Benzylmagnesium chloride was reacted with the $ZrCl_4$ complex with tetrahydrofuran ($ZrCl_4{\cdot}2THF$).[16] The yield obtained was about 80%, with respect to the reported 30%.

Cp_2TiMe_2[17] and Cp_2ZrMe_2[18] were prepared according to the reported procedure.

Ali-Bu_3 was purchased from Schering and distilled under reduced pressure. The purity was checked by ^1H NMR. A 0.1 M solution in *n*-heptane was employed in the polymerization.

$AlBz_3$ was prepared as reported in the literature.[19]

Reaction between Ethyl Benzoate and Ali-Bu_3 or $ZrBz_4$. Reaction in a Schlenk Vial. In a 250-mL Schlenk vial, 100 mL of *n*-heptane and 1.25 mL of a 0.01 M solution of ethyl benzoate in *n*-heptane were introduced and thermostated at 60 °C. A total of 1.5 mL of a 0.1 M solution of either Ali-Bu_3 or $ZrBz_4$ in *n*-heptane was then added. Samples of the reaction mixture were taken after 1, 5, 10, 15, 30, 45, and 60 min and quenched in ethanol. These samples were then injected in a Hewlett-Packard 5890 gas chromatograph, after introduction of *n*-decane as the internal standard. The amount of unreacted ethyl benzoate was calculated with respect to the internal standard. The reaction products were identified on a Finnigan Mat INCOS 50 quadrupole mass analyzer interfaced with a HP-5090 gas chromatograph.

Reaction in the NMR Tube. Reaction with $ZrBz_4$. A total of 0.20 mmol of $ZrBz_4$ was dissolved in 0.3 mL of deuterated benzene (C_6D_6). A total of 0.2 mL of a 1.11 M solution containing ethyl benzoate in C_6D_6 was then added.

Reaction with Ali-Bu_3. A total of 0.42 mmol of Ali-Bu_3 was dissolved in 0.3 mL of C_6D_6. A total of 0.19 mL of this solution and 0.1 mL of C_6D_6 were added to 0.2 mL of the above reported ethyl benzoate solution. In both reactions, ^1H NMR spectra were taken at room temperature after 5 and 60 min.

Reaction between $MgCl_2$/$TiCl_4$/Ethyl Benzoate Catalyst and Ali-Bu_3 or $ZrBz_4$. The reactions were performed according to the following general procedure. In a 2-L round-bottomed flask equipped with a mechanical stirrer, *n*-heptane and the solid catalyst were introduced and thermostated at the temperature chosen for the reaction. A solution of the cocatalyst in *n*-heptane was then added. The reaction mixture was allowed to stir for the fixed time and then quickly filtered. The recovered solid was washed with *n*-heptane four to five times.

The catalyst was then dissolved in ethanol and the solution injected in the gas chromatograph, after the addition of *n*-decane as the internal standard.

Polymerizations. Polymerizations at 0.11 or 0.12 MPa were performed in a 500-mL round-bottomed flask equipped with a magnetic stirrer, a thermometer, and valves for the introduction of catalyst, solvent, and gases.

The following standard procedure was employed in all polymerizations: a suspension of the catalyst in *n*-heptane was introduced into the flask and thermostated at the polymerization temperature. The heptane solution of the cocatalyst (0.1 M) was then added and, after 5 min, the gaseous monomer was bubbled through the polymerization suspension. The polymerization was stopped by injecting 2 mL of ethanol and the polymer recovered by precipitation with methanol/HCl.

Polymerizations at 1.01 MPa were performed in a 2-L stainless steel autoclave equipped with a magnetic stirrer, a thermocouple, and valves for the introduction of solvents and gaseous monomers. The standard procedure was as follows: a suspension of the catalyst and the cocatalyst was introduced into the autoclave and thermostated at the polymerization temperature. Hydrogen and ethylene were then added. The polymerization was stopped by degassing the monomers and then injecting 2 mL of ethanol. The polymer was recovered as reported above.

Polymer Characterization. The isotacticity index (II) of polypropylene was determined by extraction with boiling heptane in a Kumagawa extractor.

^{13}C NMR analysis was performed in $C_2D_2Cl_2$ at 110 °C on a Bruker AM300 spectrometer at 75.469 MHz. The chemical shifts were referred to the solvent chemical shift at 74.40 ppm.

Thermal analysis was carried out with a Perkin-Elmer DSC-7, in a temperature range from 20 to 200 °C at a heating rate of 20 °C/min.

The inherent viscosity of the samples was measured in a 0.25 wt % solution in tetralin at 135 °C.

Gel-permeation chromatographic (GPC) analysis was carried out by using a Waters 150-C GPC equipped with Progel TSK columns working at 135 °C in 1,2-dichlorobenzene.

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