

Unusual Synergetic Effect of Cocatalysts in the Polymerization of Propylene by a Zirconium Bis(benzamidinate) Dimethyl Complex

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Summary: The zirconium benzamidinate dimethyl complex $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{Zr}(\text{Me})_2$ (**1**) was activated by a mixture of trityl tetrakis(pentafluorophenyl)borate (TTPB) and a small amount of methylalumoxane (MAO) (Zr:B:Al = 1:1:50), forming an extremely active catalytic system for the polymerization of olefins, producing high-density polyethylene and elastomeric polypropylene with a narrow MWD. This catalytic system rivals the activity of the best nonmetallocene systems and approaches the activities of the best metallocene complexes. Single active sites are obtained only after the addition of propylene. A plausible activation mechanism is proposed, which is corroborated by NMR, ESR spectroscopy, radical trapping on fullerene, and MALDI-TOF mass spectroscopy experiments.

During the last two decades a wide exploration of new Ziegler–Natta types of homogeneous complexes, as alternative precatalysts for the polymerization of α -olefins, has been accomplished.¹ For metallocenes, besides studies on the structural effects of the ligands in the polymerization process² and thorough kinetic examinations,³ the effect of the cocatalysts has also been investigated.⁴ Recently, metallocenes have been used for the polymerizations of propylene using a combination of alkyl aluminum and perfluoroaryl borane and borate co-activators.⁵ However, in all cases the aluminum compounds were used only as scavengers and/or methylating agents.⁶

Here we report preliminary unexpected results in the polymerization of propylene by the bis(benzamidinato) zirconium dimethyl complex $[\text{PhC}(\text{NSiMe}_3)_2]_2\text{Zr}(\text{Me})_2$ (**1**), which was activated by a mixture of trityl tetrakis(pentafluorophenyl)borate (TTPB) and a small amount of methylalumoxane (MAO). This resulted in the abrupt increase of the polymerization activity (Table 1), as compared to the best results obtained for complex **1** with a large excess of MAO, rivaling the best nonmetallocene

Table 1. Polymerization Results for Complex 1 Activated by a Mixture of MAO and TTPB^a

	<i>T</i> [°C]	time [h]	<i>A</i> ^b × 10 ⁻⁴	mmmm ^c [%]	<i>M</i> _w ^d	MWD
1	30 ^e	0.06 ^f	4330	13	23 000	2.49
2	-30	3	0			
3 ^g	-10	3	15.7	11	114 000	2.03
4 ^h	-10	3	22.5	12	126 000	2.38
5	-10	3	19.5	11	131 000	2.26
6	0	0.07 ^f	3810	13	21 000	2.11
7 ⁱ	30	4	28.5	10	160 000	2.48
8 ^j	30	0.08 ^f	4180	12	19 000	2.34
9 ^k	30 ^e	0.03	1126		618 000	2.34

^a 5 mg of complex **1** (M:Al = 1:50; M:TTPB = 1:1), 6 mL of toluene, 40 mL of liquid propylene. ^b g pol × mol cat⁻¹ × h⁻¹. ^c Pentad analysis using ¹³C NMR. ^d GPC measurements. ^e Highly exothermic reaction. ^f Full conversion. ^g 2.5 mg of catalyst. ^h 10 mg of catalyst. ⁱ Reaction without TTPB, M:Al = 1:1000. ^j 60 mL of liquid propylene. ^k Ethylene, *P* = 20 atm.

systems and approaching the activities of the best metallocenes.⁷ In addition, we present a combination of ¹H, ¹³C, ²⁹Si, ¹⁹F, and ¹⁵N NMR, ESR, radical trapping using fullerene C₆₀, and MALDI-TOF studies describing the formation of the single-site active species.

Complex **1** was synthesized as described in the literature.⁸ Its activation using the TTPB boron cocatalyst and propylene did not produce any polymer. The mixture of complex **1** and TTPB produces only a brown precipitate with the concomitant elimination of 1 equiv of Ph₃CCH₃, as found in the NMR and MALDI TOF analysis.⁹ However, the addition of MAO (Zr:Al = 1:50) to the previous precipitate induces a 2 orders of magnitude increase in activity (10⁷ g PP/mol cat × h) in the polymerization of propylene, producing an elastomeric polymer, as compared to the activity obtained with complex **1** and MAO (Zr:Al ratio = 1:1000) (Table 1, entries 1 and 7)). It is important to point out that only after the addition of propylene does the reaction mixture become fully soluble, and its color changes to wine-red.

Note that without TTPB, the polymerization promoted by complex **1** and MAO (Zr:Al = 1:50) produced only negligible amounts of polymer. Moreover, replacing the MAO, in the catalytic mixture with TTPB, by tri-isobutylaluminum led to a total loss in the catalytic activity. Hence, the activation of the dimethyl complex requires the presence of MAO. These facts indicate that only the combined action of TTPB and MAO is responsible for the synergetic catalytic properties.

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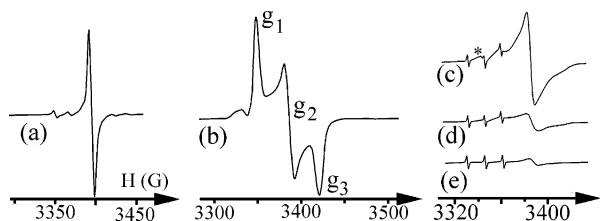


Figure 1. ESR spectrum for complex **1** with TTPB and MAO. (a) Before propylene addition at 290 K. ESR spectra were recorded for determination of the g -factor with TEMPO ($g = 2.0059$) at 290 K (see Supporting Information). (b) At 150 K. (c) After the first back-filling of the ESR tube, calibrated with TEMPO. The signal with an asterisk is an organic radical. (d) After 6 back-fillings. (e) After 12 back-fillings.

To shed some light on the identity of the active species, we have monitored the activation process using a combination of physical methods. Following the activation process of complex **1** with TPPB and MAO, via ^{19}F NMR,⁹ revealed that no signal changes are observed until the addition of propylene to the reaction mixture. After a small amount of propylene was added, some new signals were observed. However, those signals disappeared when enough propylene was added, and a new shifted set of signals for the counterion $\text{B}(\text{C}_6\text{F}_5)_4^-$ was exhibited. These results allow us to conclude that propylene induces the formation of the active species.

^{15}N HMBC and ^{29}Si HMBC 2D-NMR spectra⁹ indicate only one kind of nitrogen and one kind of silicon atom in the active species. Both atoms are correlated to the same TMS signal in the ^1H NMR spectrum. These results, together with the narrow MWD observed (Table 1), indicate the formation of a single-site catalyst. Corroborating these findings, the fractionation of the polymer produced only one fraction. Furthermore, the observed ^{29}Si signal appears at a different chemical shift from the corresponding signal for the aluminum benzamidinate dichloro or dimethyl complexes,¹⁰ indicating the lack of migration of the ancillary ligand to the MAO.

The formation of Zr(III) derivatives was tracked by ESR. An ESR signal was observed for the mixture of complex **1** with TTPB and MAO (Figure 1a), whereas for either the neat complex or its mixture with TTPB no signal was detected. The ESR spectrum shows a single line at $g = 1.979$ with satellites due to the interaction of the unpaired electron with magnetic isotopes ^{91}Zr nucleus ($a = 19.3$ G, ^{91}Zr , 11.23%, $I = 5/2$).¹¹ The signal in frozen glasses (150 K) is characterized by a strong anisotropy of the g -factor (Figure 1b), which results in three ESR signals, indicating the nonplanarity of the molecule ($g_1 = 2.003$, $g_2 = 1.980$, $g_3 = 1.960$).¹¹

The intensity of the ESR signal disappeared progressively upon the addition of propylene. A stable organic radical ($g = 2.003$ broad signal), presumably of polymeric nature, was initially formed only after the first aliquot of propylene was added (Figure 1c; the signal is marked with an asterisk). This signal also vanished after a further supplement of propylene. These results indicate that propylene induces the oxidation of Zr(III) to Zr(IV) similarly to other observed group IV allylic complexes.¹² Furthermore, the formation of a $[\text{Zr}-\text{H}]^+$ signal

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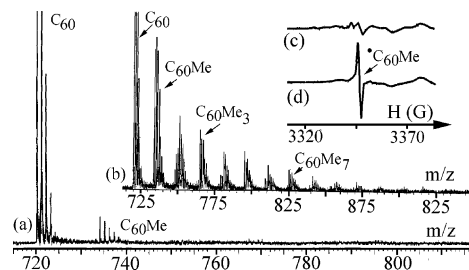


Figure 2. MALDI-TOF analysis of sample prepared from complex **1**, TTPB, and MAO using fullerene as a radical trapping agent, at different catalyst concentrations: (a) 2 mg/mL of **1**; (b) 10 mg/mL of **1**; (c) ESR spectra of reaction mixture (2 mg/mL of **1**); (d) ESR spectra of reaction mixture (2 mg/mL of **1**) under visible light ($\lambda > 600$ nm).

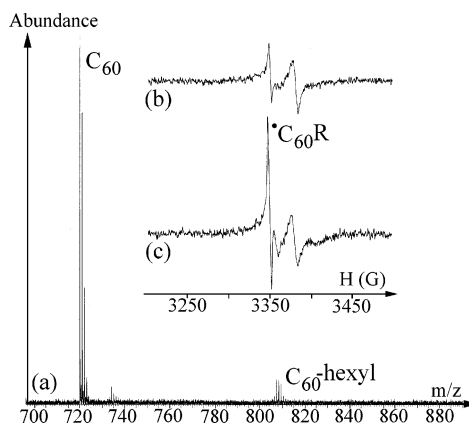


Figure 3. Reaction between titanium benzimidate complex **2**, TTPB, and MAO using fullerene as a radical trapping agent: (a) MALDI-TOF analysis of the reaction mixture; (b) ESR spectra of the reaction mixture; (c) ESR spectra of the reaction mixture under visible light ($\lambda > 600$ nm).

can be observed ($\delta_{\text{H}} = -2.50$ ppm) only after the addition of propylene, with no NMR correlations to ^{13}C , ^{15}N , ^{29}Si , and ^{11}B nuclei.

To shed some light on the nature of the organic radical and the Zr(IV) \rightarrow Zr(III) process, experiments with [60]fullerene (C_{60}), used as a radical trapping agent, were performed.¹³ In the first experiment, the fullerene was mixed with complex **1** and TTPB before the addition of MAO to trap the corresponding organic radicals that may be formed upon the reduction of the metal, and the results are presented in Figure 2.

According to MALDI-TOF analysis of the sample, a methyl radical was trapped (Figure 2a). Interestingly, the amount of the methyl radicals trapped was dependent on the catalyst concentration, indicating that the zirconium complex (not MAO!) was the radical source (compare parts a and b of Figure 2). To observe any trapping moieties, the irradiation of the sample in the ESR cavity by visible light ($\lambda > 600$ nm) was performed, giving rise only to the reversible dissociation of the dimeric fullereryl radicals.



A similar trapping experiment was performed to elucidate the oxidation of Zr(III) \rightarrow Zr(IV) by propylene. In this experiment, the fullerene was added only after the complete formation of the Zr(III) complex to prevent the trapping of any methyl radicals. ESR analysis shows the formation of a small, very broad organic signal (intensifies after irradiation); however MALDI TOF experiments showed neither a fullerene signal nor

