Increase of Catalyst Activity by Transfer of Bulky Alkyl Groups from Zirconocene Complexes to Methylalumoxane

Christine E. Denner, Helmut G. Alt

Laboratorium für Anorganische Chemie, Universität Bayreuth, Postfach 101251, D-95440 Bayreuth, Germany

ABSTRACT: The activity of metallocene catalysts in ethylene polymerization can be increased by a factor of up to 3.5 when the corresponding metallocene catalyst precursors possess one or two bulky alkyl ligands such as benzyl groups instead of the conventional chloro ligands. We assume that in the activation process with methylalumoxane (MAO) these bulky alkyl groups are transferred from the metal to the MAO cocatalyst. The actual cocatalyst is supposed to be a cage with one or more monomeric $AlMe_3$ molecules inside. The bulky alkyl group is transferred to such an $AlMe_3$ unit and can act as a spacer separating the catalytically active metallocenium cation from the MAO anion. This effect is supposed to be responsible for the increase in activity. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1336–1340, 2003

Key words: zirconocene complexes; ethylene polymerization

INTRODUCTION

The classical activator for metallocene catalyst precursors is methylalumoxane (MAO).[1–10] The activation step can proceed in the following manner[11]:
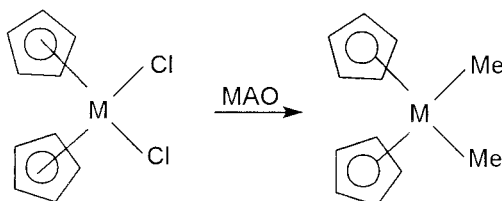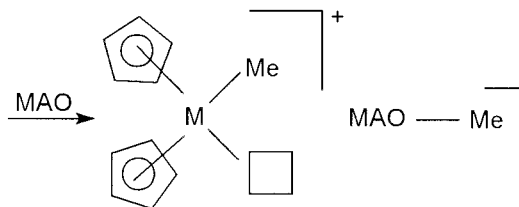

The cationic metallocenium complex is supposed to be the actual catalyst.[12–14] The exact role of MAO is still unknown except that it works as a methylating agent and then abstracts a methyl anion from the metal to form such cationic species.

From recent studies it became obvious that MAO consists of a variety of linear and cyclic oligomers that are in a dynamic equilibrium.[8,9,11]

The actual cocatalysts are supposed to be MAO cages with monomeric $AlMe_3$ molecules inside that are able to perform the above-mentioned reactions.[4–6] To provide more proof for this hypothesis, we synthesized zirconocene complexes with bulky alkyl groups. These groups should affect the activation process with MAO and should have an influence on the catalyst properties in ethylene polymerization.

EXPERIMENTAL

NMR spectroscopy

A Bruker NMR instrument ARX 250 was available for recording NMR spectra. The organometallic samples were placed in the NMR tubes under argon and measured at 25°C. The chemical shifts in ^{1}H-NMR spectra were referred to the residual proton signal of the solvent ($\delta = 7.15$ ppm for benzene) and in ^{13}C-NMR spectra to the solvent signal ($\delta = 128.0$ ppm for benzene-d_6).

General synthesis procedure for Grignard reagents

The procedure for synthesis of Grignard reagents was as follows: To a mixture of 0.01 g of Mg (0.41 mmol) in 40 mL of ether, the corresponding bromide was added dropwise. The residue of Mg was filtered, and the solution was used for further reactions.

For synthesis of a chloride Grignard, 0.01 g of Mg (0.41 mmol) was reacted with the corresponding chloride (0.03 mmol).

Correspondence to: H. G. Alt (helmut.alt@uni-bayreuth.de).

Synthesis of complexes 2–6

In 50 mL of toluene, 1 g of Cp_2ZrCl_2 (3.4 mmol) was dissolved. The corresponding chloride Grignard (3.4 mmol) was added and stirred for 5 h. The solution was filtered over sodium sulfate and the solvent evaporated. The residue was washed twice with 50 mL of pentane and evaporated. The yields were 45%–50%.

Synthesis of complexes 7–11

In 50 mL of toluene, 1 g of Cp_2ZrCl_2 (3.4 mmol) was dissolved. The corresponding bromide Grignard (6.8 mmol) was added and stirred overnight. After filtration of the solution over sodium sulfate, the solvent was evaporated. The residue was washed with 100 mL of pentane and the solvent evaporated. The yields were 40%–50%.

Homopolymerization of ethylene

In a 1-L Büchi laboratory autoclave was placed 500 mL of *n*-pentane. This was mixed with the catalyst solution, and the autoclave was thermostated at 60°C. An ethylene pressure of 10 bar was applied. The mixture

was stirred for 1 h at 60°C, and the reaction terminated by releasing the pressure in the reactor. The obtained polymer was dried *in vacuo*.
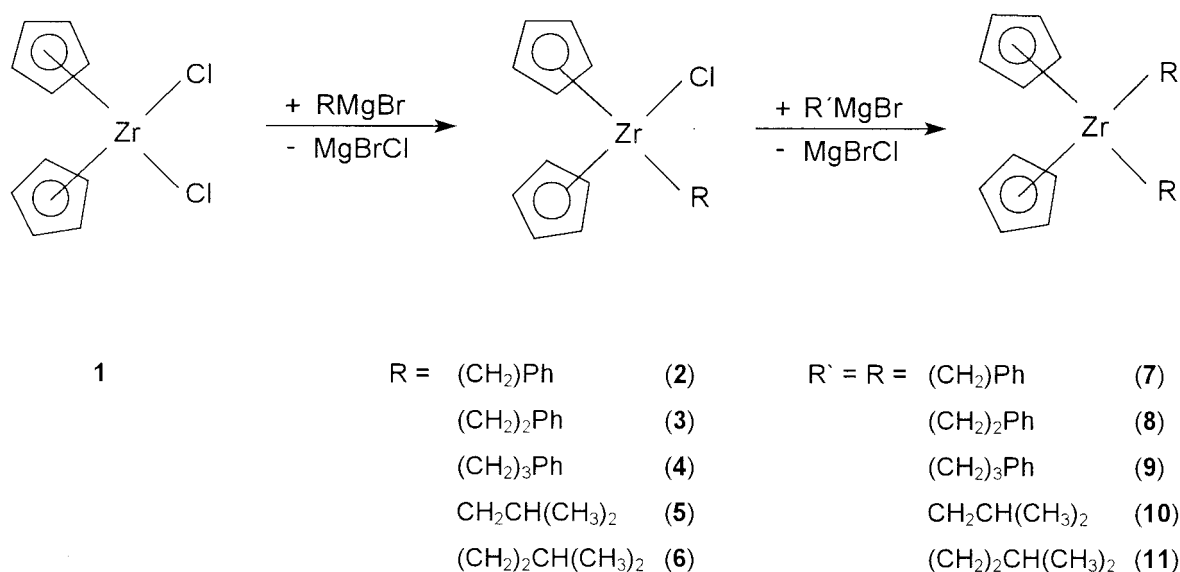
Heteropolymerization of ethylene

To the activated catalyst precursor solution, 1 g of silica per μmol of catalyst precursor was added and placed in a 1-L Büchi laboratory autoclave with 500 mL of *n*-pentane. The autoclave was thermostated at 60°C, and an ethylene pressure of 10 bar was applied. After stirring for 1 h at 60°C, the reaction was terminated by releasing the pressure in the reactor. The obtained polymer was dried *in vacuo*.

RESULTS AND DISCUSSION

Synthesis and characterization of zirconocene complexes with bulky carbyl ligands

The synthesis of zirconocene complexes with bulky alkyl ligands can be performed by the reaction of a metallocene dichloride complex and the corresponding Grignard reagent.[15] Depending on the stoichiometric amount of the Grignard reagent mono- or disubstituted complexes can be obtained:

1	R =	$(CH_2)Ph$	**(2)**	R` = R =	$(CH_2)Ph$	**(7)**
		$(CH_2)_2Ph$	**(3)**		$(CH_2)_2Ph$	**(8)**
		$(CH_2)_3Ph$	**(4)**		$(CH_2)_3Ph$	**(9)**
		$CH_2CH(CH_3)_2$	**(5)**		$CH_2CH(CH_3)_2$	**(10)**
		$(CH_2)_2CH(CH_3)_2$	**(6)**		$(CH_2)_2CH(CH_3)_2$	**(11)**

Complexes **2–11** are all diamagnetic and were characterized by ^{1}H- and ^{13}C-NMR spectroscopy (Table I).

Homogeneous and heterogeneous polymerization of ethylene

Complexes **1–12** were activated with an excess of MAO in homogeneous solution and used for ethylene polymerization. The polymerization parameters such as the Zr/Al ratio (1:2500), the temperature (60°C), the ethylene pressure (10 bar), and the volume of the

solvent pentane (500 mL) were kept constant for all polymerization experiments.

In a second series of experiments the same catalysts were heterogenized on silica, and the activities for ethylene polymerization were determined under identical reaction conditions. The results are given in Table II.

Discussion of polymerization results

It was a surprise to observe a considerable increase in catalyst activity when zirconocene complexes

TABLE I
NMR Characterization of Complexes 2–11

Complex	^{1}H-NMR[a]	^{13}C-NMR[b]
2[16]	7.32–7.13(m, 5H), 5.74(s, 10H), 2.11 (s 2H)	151.8 (Cq), 128.3 (CH), 127.6 (CH), 121.8 (CH), 113.4 (CH), 62.3 (CH$_2$)
3[17]	7.13–7.26 (m, 5H), 5.87 (s, 10H), 2.90 (m, 2H), 1.19 (m, 2H)	132.4 (Cq), 128.7 (CH), 127.2 (CH), 125.5 (CH), 112.8 (CH), 58.6 (CH$_2$), 40.5 (CH$_2$)
4	7.35–7.27 (m, 5H), 5.79 (s, 10H), 2.60 (m, 2H), 1.90 (m, 2H), 0.91 (m, 2H)	140.0 (Cq), 128.9 (CH), 127.6 (CH), 126.9 (CH), 112.5 (CH), 57.7 (CH$_2$), 45.2 (CH$_2$), 36.1 (CH$_2$)
5[18]	5.79 (s, 10H), 2.15 (m, 1H), 0.99 (d, 6H), 0.82 (d, 2H)	110.9 (CH), 70.8 (CH$_2$), 33.4 (CH), 27.6 (CH$_3$), 24.5 (CH$_3$)
6[19]	5.75 (s, 10H), 2.05 (m, 1H), 1.17 (m, 2H), 0.93 (d, 6H), 0.78 (m, 2H)	109.8 (CH), 68.8 (CH$_2$), 42.3 (CH$_2$), 31.9 (CH), 25.7 (CH$_3$), 22.1 (CH$_3$)
7[16]	7.25–7.08 (m, 10H), 5.68 (s, 10H), 1.99 (s, 4H)	145.3 (Cq), 127.9 (CH), 126.8 (CH), 120.2 (CH), 112.8 (CH), 59.4 (CH$_2$)
8[17]	7.19–7.03 (m, 10H), 5.79 (s, 10H), 2.66 (m, 4H), 0.99 (m, 4H)	131.3 (Cq), 128.2 (CH), 126.8 (CH), 124.8 (CH), 112.5 (CH), 55.4 (CH$_2$), 38.7 (CH)
9	7.23–6.99 (m; 10H), 5.71 (s, 10H), 5.54 (m, 2H), 1.77 (m, 2H), 0.86 (m, 2H)	139.8 (Cq), 128.9 (CH), 127.0 (CH), 126.4 (CH), 112.2 (CH), 56.4 (CH$_2$), 43.1 (CH$_2$), 33.2 (CH$_2$)
10	5.68 (s, 10H), 2.02 (m, 2H), 0.86 (s, 12H), 0.76 (d, 4H)	110.2 (CH), 68.2 (CH$_2$), 30.2 (CH), 20.2 (CH$_3$)
11	5.66 (s, 10H), 2.00 (m, 2H), 1.11 (m, 4H), 0.86 (s, 12H), 0.66 (m, 4H)	109.2 (CH), 66.5 (CH$_2$), 40.1 (CH$_2$), 29.8 (CH), 20.9 (CH$_3$)

[a] 25°C, in benzene-d$_6$, δ (ppm) rel. benzene (7.15).
[b] 25°C, in benzene-d$_6$, δ (ppm) rel. benzene (128.0).

with bulky alkyl ligands were used for catalytic ethylene polymerization. It was assumed that it would not make any difference whether a zirconocene dichloride or a zirconocene dialkyl complex was used as a catalyst precursor because the active species is supposed to be the zirconocene monomethyl cation, $[Cp_2ZrMe]^+$, in all cases when MAO is used as a cocatalyst. Obviously, the nature of the MAO counterion plays a significant role that cannot be ignored.

Because MAO consists of a variety of species in dynamic equilibrium with each other, only the species responsible for the activation step should be of concern. Such a species is supposed to be a cage-type MAO[4–6,21] that contains one or more monomeric AlMe$_3$ units.

The AlMe$_3$ groups in the cage are able to perform the methylation and subsequent methylanion abstraction in the activation process. Zirconocene complexes with bulky alkyl ligands are activated in a similar manner except that instead of a methyl group, a spacious organyl group is transferred from the metal to the MAO cage. As a consequence, the metallocenium cation and the MAO anion are separated more efficiently, thus increasing the activity of the catalyst because the monomer has better access to the active

TABLE II
Polymerization Results

Catalyst precursor	Homogeneous catalysis[a]			Heterogeneous catalysis[b]		
	Activity [kg PE/g Zrh]	M_w [g/mol]	D [M_w/M_n]	Activity [kg PE/g Zrh]	M_w [g/mol]	D [M_w/M_n]
1	150	290,000	n.d.	75	270,000	n.d.
2	590	337,500	3.091	390	305,000	3.121
3	470	353,000	3.271	190	298,000	3.608
4	450	363,000	3.321	180	283,000	3.911
5	200	346,000	3.194	80	295,000	3.428
6	185	352,000	3.216	60	288,000	3.609
7	610	290,000	2.991	410	275,000	3.012
8	500	284,000	2.813	230	234,000	3.061
9	450	321,000	3.211	205	231,000	3.153
10	245	330,000	2.994	110	255,000	2.778
11	210	340,000	2.765	75	275,000	2.698
12	160	—	—	85	—	—

[a] T_p = 60°C; solvent: 500 mL of pentane, 10 bar ethylene pressure; [Zr]/[Al] = 1:2500.
[b] T_p = 60°C; solvent: 500 mL of pentane, 10 bar ethylene pressure; [Zr]/[Al] = 1:1500; 1 g silica/μmol Zr. n.d. = not determined.

center and the growing polymer chain has more space for its orientation.

At this point, it cannot be concluded whether this bulky organyl group acts as a bridging ligand between Zr and Al, as indicated in Figure 1, or whether it is a substituent at any other position of the cage because of the dynamic equilibrium of such systems.

Indeed, when zirconocene complexes with two bulky alkyl ligands are applied, at least one of them is supposed to end up as a substituent on the MAO cage. We observed a similar spacer effect earlier when we made the metallocene unit in ansa bis(fluorenyl) complexes so bulky that the MAO counter anion was separated from the cation.[22] Methyl substituents on the 4 and/or 5 position of the fluorenyl ligand increased the activity for ethylene polymerization by a factor of 4.5.
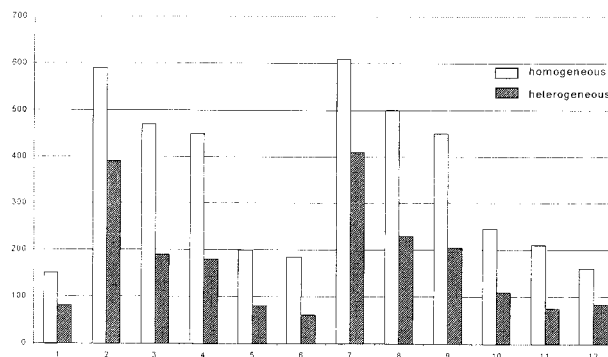
In the series of catalyst precursors **1–12** the di(benzyl) derivative **7** showed the highest activity (610 kg PE/g Zrh) in ethylene polymerization and the isopentyl(chloro) derivative **6** the lowest activity (185 kg PE/g Zrh) (Fig. 2). This is still better than the activity of the parent di(chloro) complex **1** (150 kg PE/g Zrh) and the dimethyl complex **12** (160 kg PE/g Zrh).

The chain length of the alkyl ligand also somewhat influences the activity: the longer the chain, the lower the activity. This speaks for the bridging position of the alkyl ligand in the activated catalyst. The favorable spacer effect and a disadvantageous steric crowding compete with each other.

These modified MAO anions also have an effect on the molecular weight of the produced polyethylene: the longer the chain length of the alkyl groups, the higher the molecular weight. This result indicates that the cocatalyst indeed has an influence on chain termination (β-H elimination) during the polymerization process.
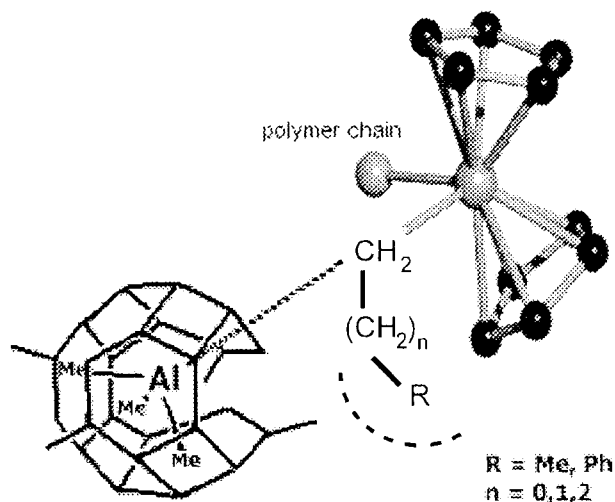
Figure 2 Activities of various metallocene catalysts in homogeneous and heterogeneous ethylene polymerization.

A comparison of homogeneous and heterogeneous ethylene polymerization confirmed earlier findings: the activity of heterogeneous catalysts dropped when silica was used as support because of the Lewis basic properties of the silica surface.

Enhancement of the activity of the metallocene catalysts can also be achieved when substituted aluminoxanes are applied as cocatalysts[23]: The incorporation of branched alkylaluminum groups into MAO results in increasing catalyst activity.

It is also known that trisisobutyl aluminum (TIBA) can have such a positive effect on the activity of the resulting catalysts.[24] Even metallocene complexes with phenoxy or siloxy ligands can be activated with MAO to impart the catalysts with greater activity than the parent complex **1**.[25,26]

We interpret all these results with the spacer effect of these bulky organyl groups.

This approach to increasing a catalyst's activity by factors of 3–4 is so attractive because it does not require isolating the corresponding di(organyl)metallocene complexes. They can be generated *in situ* and then reacted further with conventional MAO.

Different from metallocene catalysts, the half-sandwich complexes $(C_5Me_5)TiR_3$ (R = Me, Et, Bu, Bz) have an opposite effect in the catalytic polymerization of styrene[27]: the bulkier the alkyl ligands, R, the lower the activity. In this case, obviously, the disadvantageous steric hindrance from the bulky cocatalyst for the styrene monomer dominates the favorable spacer effect of the cocatalyst.

Figure 1 Interaction of a bulky alkyl group with a metallocene catalyst and the MAO cage.

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