

# Activation of Metallacycloprenes, five-membered Metallacyclocumulenes and Metallacyclopentyne of Zirconium with $i\text{-Bu}_2\text{AlH}$

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**Summary:** The recently described reaction products of zirconacycloprenes  $\text{Cp}'_2\text{Zr}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  and five-membered zirconacyclocumulenes (zirconacyclopenta-2,3,4-trienes)  $\text{Cp}'_2\text{Zr}(\eta^4\text{-1,2,3,4-RC}_4\text{R})$ ,  $\text{Cp}' = \eta^5\text{-pentamethylcyclopentadienyl}$ ,  $\text{R} = \text{Me}$ ,  $\text{Me}_3\text{Si}$  and  $\text{Ph}$ , with  $i\text{-Bu}_2\text{AlH}$  are active catalysts in the polymerization of ethylene and in the ring opening polymerization of  $\epsilon$ -caprolactone. Here we describe the different activity of these complexes after thermal activation or if additional  $i\text{-Bu}_2\text{AlH}$  together with water are added. These results are compared to those which were obtained with the complexes  $\text{Cp}_2\text{Zr}(\eta^4\text{-1,2,3,4-H}_2\text{C}_4\text{H}_2)$ ,  $\text{rac-}(\text{EBTHI})\text{ZrF}_2$ ,  $\text{rac-}(\text{EBTHI})\text{ZrCl}_2$ ,  $[\text{rac-}(\text{EBTHI})\text{Zr}(\text{H})(\mu\text{-H})]_2$  and  $\text{rac-}(\text{EBTHI})\text{Zr}(\text{F})\text{CH}_2\text{-CH}_2(2\text{-Py})$  after activation with  $i\text{-Bu}_2\text{AlH}$  together with water.

**Keywords:** ethylene polymerization; organoaluminum compounds; titanocene; zirconocene

## Introduction

In group 4 metallocene chemistry Lewis acids such as certain organoaluminum compounds can abstract alkyl groups from metallocene alkyl compounds to form coordinatively unsaturated cationic alkyl metal complexes  $[\text{Cp}'_2\text{MR}]^+$  ( $\text{Cp}' = \text{substituted or nonsubstituted } \eta^5\text{-cyclopentadienyl ligands}$ ) to give active Ziegler/Natta catalysts for olefin polymerization.<sup>[1]</sup> Mostly metallocene dihalides  $\text{Cp}'_2\text{MX}_2$  were investigated, formed by alkylation with organoaluminum compounds as activators mono-  $\text{Cp}'_2\text{M}(\text{X})\text{R}$  or dialkylated  $\text{Cp}'_2\text{MR}_2$  metallocene complexes.<sup>[2]</sup> Methylalumoxane (MAO), as partially hydrolyzed  $\text{Me}_3\text{Al}$ , is the mostly used activator in these processes.<sup>[3]</sup> More recently, isobutylalumoxane (IBAO), as partially hydrolyzed  $i\text{-Bu}_3\text{Al}$ , became inter-

esting as a cheaper alternative for an activator.<sup>[4]</sup>

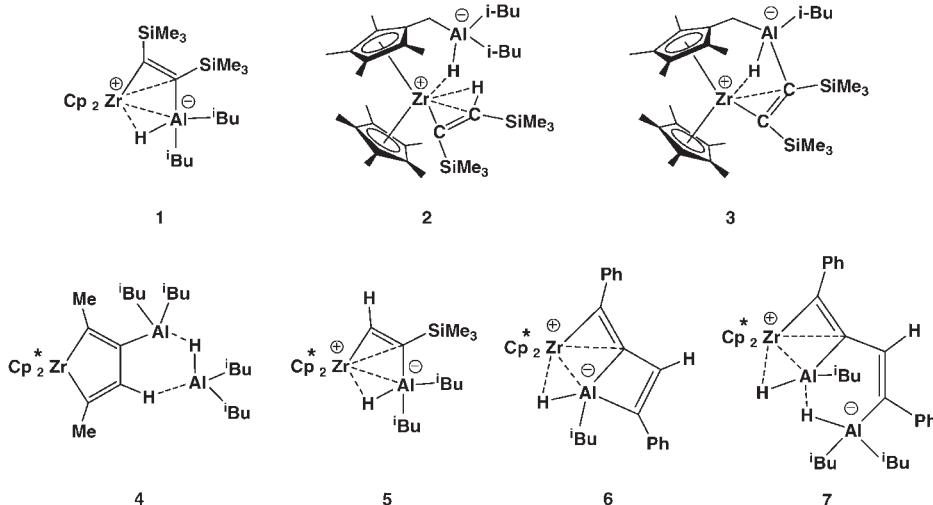
We studied instead of  $\text{Cp}'_2\text{MR}_2$  similar reactions of metallacycles, such as metallacycloprenes  $\text{Cp}'_2\text{M}(\eta^2\text{-RC}_2\text{R})$ , metallacyclopentanes  $\text{Cp}'_2\text{Zr}(\eta^2\text{-C}_4\text{R}_8)$ , metallacyclocumulenes (metallacyclopentatrienes)  $\text{Cp}'_2\text{M}(\eta^4\text{-RC}_4\text{R})$  and metallacyclopentyne  $\text{Cp}'_2\text{M}(\eta^4\text{-RC}_4\text{R})$ , all having two metal carbon  $\sigma$ -bonds, with Lewis acids, too.<sup>[5]</sup> In this context  $i\text{-Bu}_2\text{AlH}$  was investigated as a cheaper activator.

The zirconacycloprenes  $\text{Cp}'_2\text{Zr}(\eta^2\text{-Me}_3\text{SiC}_2\text{SiMe}_3)$  react with  $i\text{-Bu}_2\text{AlH}$  producing different bimetallic compounds **1–3**.<sup>[6,7]</sup> The metallacycloprenes alone or in combination with  $i\text{-Bu}_3\text{Al}$  or  $i\text{-Bu}_2\text{AlH}$  are active catalysts for the ring opening polymerization of lactones, lactames and cyclic carbonates.<sup>[6,8,9]</sup> It is worth to mention that in all these systems  $i\text{-Bu}_3\text{Al}$  smoothly forms  $i\text{-Bu}_2\text{AlH}$  which subsequently reacts, giving a chance to come to well-defined complexes. This is the reason why we did all experiments with  $i\text{-Bu}_2\text{AlH}$  as activator.

The five-membered zirconacyclocumulenes<sup>[5]</sup> (zirconacyclopenta-2,3,4-trienes)

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Scheme 1.

$\text{Cp}^*2\text{Zr}(\eta^4\text{-1,2,3,4-RC}_4\text{R})$ ,  $\text{Cp}^* = \eta^5\text{-penta-methyl-cyclopentadienyl}$ ,  $\text{R} = \text{Me}$ ,  $\text{Me}_3\text{Si}$  and  $\text{Ph}$ , reacted differently with  $i\text{-Bu}_2\text{AlH}$  with formation of complexes **4–7**.<sup>[10]</sup> The obtained complexes are efficient activators in the polymerization of olefins and  $\epsilon$ -caprolactone.<sup>[10]</sup> Starting from 1-metallacyclo-pent-3-ynes  $\text{Cp}_2\text{M}(\eta^4\text{-1,2,3,4-H}_2\text{C}_4\text{H}_2)$  ( $\text{M} = \text{Ti}$ <sup>[11]</sup>,  $\text{Zr}$ <sup>[12]</sup>(**8**)) and  $i\text{-Bu}_2\text{AlH}$  no defined complexes were isolated so far.

In this paper we report on additional conducted experiments in which the well-known ethylene polymerization, initiated by the complexes **1–5** and **7** alone,<sup>[10]</sup> was modified by the thermal activation or addition  $i\text{-Bu}_2\text{AlH}$  together with water. These results were compared with results in which the complexes  $\text{Cp}_2\text{Zr}(\eta^4\text{-1,2,3,4-H}_2\text{C}_4\text{H}_2)$  (**8**), *rac*-(EBTHI) $\text{ZrF}_2$  (**9**),<sup>[13]</sup> *rac*-(EBTHI) $\text{ZrCl}_2$  (**10**),<sup>[14]</sup> [*rac*-(EBTHI)- $\text{Zr}(\text{H})(\mu\text{-H})_2$ ] (**11**)<sup>[15]</sup> and *rac*-(EBTHI)- $\text{Zr}(\text{F})\text{CH}_2\text{-CH}_2(2\text{-Py})$  (**12**)<sup>[16]</sup> were activated by the addition of  $i\text{-Bu}_2\text{AlH}$  together with water, too. Additionally, the complexes *rac*-(EBTHI) $\text{ZrF}_2$  (**9**), *rac*-(EBTHI)- $\text{ZrCl}_2$  (**10**) and *rac*-(EBTHI)- $\text{ZrMe}_2$  (**13**)<sup>[17]</sup> were activated by MAO to understand the importance of alkylation for the formation of these active catalysts.

## Results and Discussion

Investigations on catalytic activity of the complexes **1–5** and **7** in ethylene polymerization showed that only complex **7** catalyzed the polymerization at 40 °C, and complexes **1–5** were not active under these conditions. Addition of the tenfold excess of  $i\text{-Bu}_2\text{AlH}$  did not lead to higher activity of complexes **1–5**, and the complex **7** lost its activity. However, most of these complexes catalyzed the ethylene polymerization after thermal activation or after controlled addition of water to the mixture of complexes and  $i\text{-Bu}_2\text{AlH}$ .

For thermal activation the complexes **1–5** were heated at 90 °C in the ethylene atmosphere for 1.5–2 h leading firstly to no polymerization. After cooling the reaction mixture to room temperature under continuous stirring, a rapid formation of polymer were observed in the case of complexes **2–5**.

Another way to activate the catalysts **1–5** and **7** was to add 5 equivalents of water to the mixture of complexes and 10 equivalents of  $i\text{-Bu}_2\text{AlH}$  in toluene. This also caused the intensive formation of polyethylene (see Table 1). The ratio of *i*-

**Table 1.**

Ethylene Polymerization by complexes **1–5** and **7** alone, activated by thermal activation, 10 equivalents of *i*-Bu<sub>2</sub>AlH or 10 equivalents of *i*-Bu<sub>2</sub>AlH together with 5 equivalents of H<sub>2</sub>O

Complexes	Activity in kg polyethylene / (mol · h) <sup>[a]</sup>		
	Complex	Complex +10 <i>i</i> -Bu <sub>2</sub> AlH	Complex +10 <i>i</i> -Bu <sub>2</sub> AlH + 5 H <sub>2</sub> O
<b>1</b>	0	0	traces
	0 <sup>[b]</sup>	0 <sup>[b]</sup>	–
<b>2</b>	0	0	69
	55 <sup>[b]</sup>	57 <sup>[b]</sup>	–
<b>3</b>	0	0	85
	0 <sup>[b]</sup>	8 <sup>[b]</sup>	–
<b>4</b>	0	0	96
	220 <sup>[b]</sup>	182 <sup>[b]</sup>	–
<b>5</b>	0	0	108
	105 <sup>[b]</sup>	201 <sup>[b]</sup>	–
<b>7</b>	100	0	84

<sup>[a]</sup> 1.1 bar, 15 min; 0.04 mmol of complex in 20 mL toluene

<sup>[b]</sup> activated 1.5–2 h at 90 °C in ethylene atmosphere

Bu<sub>2</sub>AlH to H<sub>2</sub>O (2: 1) was found to be best for highest activity in the case of complex **9** (see below, Table 3 and Figure 1). It is difficult to rationalize all these results at the moment, but one has to assume that the addition of water leads to “IBAO-like species”.

These results were compared with those in which the complexes Cp<sub>2</sub>Zr(η<sup>4</sup>-1,2,3, 4-H<sub>2</sub>C<sub>4</sub>H<sub>2</sub>) (**8**), *rac*-(EBTHI)ZrF<sub>2</sub> (**9**), *rac*-(EBTHI)ZrCl<sub>2</sub> (**10**), [*rac*-(EBTHI)Zr(H)- (μ-H)<sub>2</sub>] (**11**) and *rac*-(EBTHI)Zr(F)CH<sub>2</sub>-CH<sub>2</sub>(2-Py) (**12**) were activated by the addition of *i*-Bu<sub>2</sub>AlH together with water (Table 2). The reaction with *i*-Bu<sub>2</sub>AlH gave

no activity for all complexes without water. Together with water one can see that the fluoride **9** is more active compared to the chloride **10**. Formation of the hydride **11** in the reaction of the fluoride **9** with *i*-Bu<sub>2</sub>AlH is well-established,<sup>[18]</sup> and this could be the reason why the hydride is similarly active. The highest activity was found for the monofluoride **12**. A reason for this could be the process of alkylation which is for complex **12** partially realized before the activation (in contrast to the other complexes).

For a better understanding of the influence of water, the ethylene polymerization by complex **9** alone, and activated by 10 equivalents of *i*-Bu<sub>2</sub>AlH together with different equivalents of H<sub>2</sub>O (Table 3) was investigated. With 5 equivalents of water and 10 equivalents of *i*-Bu<sub>2</sub>AlH the maximum of activity was found. It is difficult to understand all these results in detail, but as in the above discussed case one can assume here the formation of IBAO, too. As well-known for MAO, the reaction of *i*-Bu<sub>2</sub>AlH with water formed “IBAO-like species” led to higher activities in ethylene polymerization for different systems used.

To verify if the process of the alkylation is important for the activity of the systems, we compared the dihalides **9** and **10** to the dimethyl complex *rac*-(EBTHI)ZrMe<sub>2</sub> (**13**) after activation by MAO. What we found was a higher activity for complex **13** compared to **9** and **10**. This result could be important for two points. The first is that the alkylation process is likely really very important and the above discussed reason

**Table 2.**

Ethylene Polymerization by complexes **8**, **9**, **10** and **11**, activated by 10 equivalents of *i*-Bu<sub>2</sub>AlH or 10 equivalents of *i*-Bu<sub>2</sub>AlH together with 5 equivalents of H<sub>2</sub>O

Complexes	Activity in kg polyethylene / (mol · h) <sup>[a]</sup>		
	Complex	Complex	Complex
	+10 <i>i</i> -Bu <sub>2</sub> AlH	+10 <i>i</i> -Bu <sub>2</sub> AlH	+5 H <sub>2</sub> O
Cp <sub>2</sub> Zr(η <sup>4</sup> -1,2,3,4-H <sub>2</sub> C <sub>4</sub> H <sub>2</sub> ) ( <b>8</b> )	0	–	Traces
<i>rac</i> -(EBTHI)ZrF <sub>2</sub> ( <b>9</b> )	0	–	53
<i>rac</i> -(EBTHI)ZrCl <sub>2</sub> ( <b>10</b> )	0	–	14
[ <i>rac</i> -(EBTHI)ZrH] <sub>2</sub> ( <b>11</b> )	0	–	34
<i>rac</i> -(EBTHI)Zr(F)CH <sub>2</sub> CH <sub>2</sub> (2-Py) ( <b>12</b> )	–	–	57

<sup>[a]</sup> 1.1 bar, 15 min; 40 °C; 0.08 mmol of complexes, 0.8 mmol of *i*-Bu<sub>2</sub>AlH and 0.4 mmol of H<sub>2</sub>O in 20 mL of toluene

**Table 3.**

Ethylene Polymerization by complex **9** activated by 10 equivalents of *i*-Bu<sub>2</sub>AlH together with different equivalents of H<sub>2</sub>O

Equivs. of H <sub>2</sub> O/10 equivs. of <i>i</i> -Bu <sub>2</sub> AlH	Activity in kg polyethylene/(mol · h) <sup>[a]</sup>
0	0
1	23
2	33
3	45
4	43
5	53
7.5	44
10	34

<sup>[a]</sup> 1.1 bar, 15 min; 40 °C; 0.08 mmol of *rac*-(EBTHI)ZrF<sub>2</sub> and 0.8 mmol of *i*-Bu<sub>2</sub>AlH in 20 mL of toluene

for the higher activity of **12** is right. Additionally, this could give an explanation why complexes **4**, **5** and **7** with Zr-C bonds are most active complexes of this work. Second is, that the formed Zr-H bonds of the hydride complexes **5**, **7** and **12** alone do not initiate the ethylene polymerization.

## Experimental Part

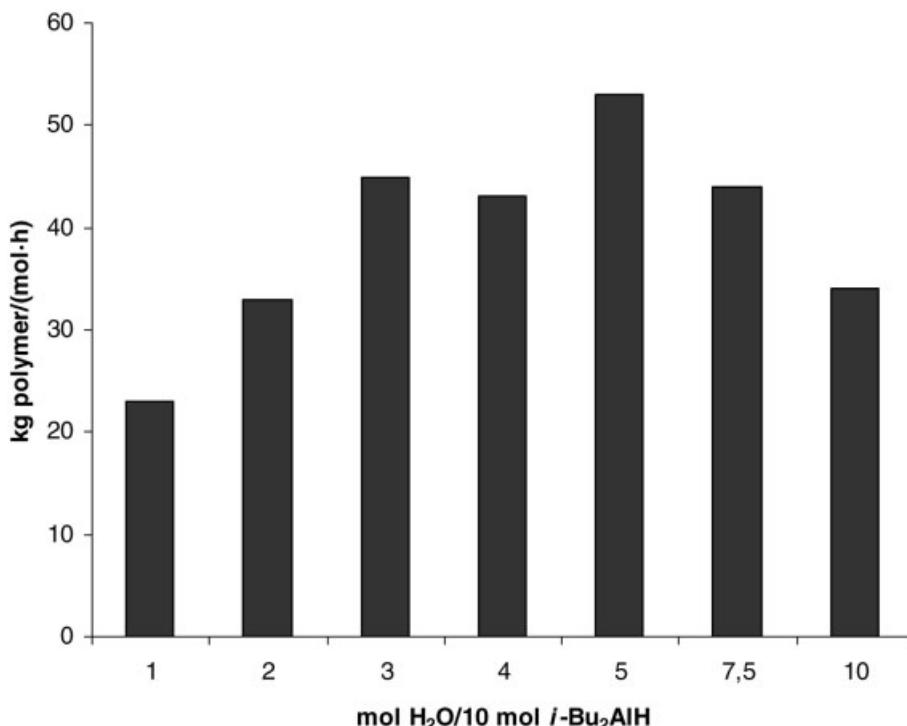
### Polymerization of Ethylene

#### General Procedure

Complex **1–5** or **7** (0.04 mmol) was dissolved in 20 mL of toluene under argon. The inert gas was carefully removed in vacuum, and the flask with the solution was filled with ethylene (1.1 bar). The solution was stirred for 15 min at 40 °C. After 15 min the ethylene was removed. The polymer was filtered, washed with toluene and dried in vacuo.

#### Thermal Activation

Complex **1–5** (0.04 mmol) was dissolved in 20 mL of toluene under argon. The inert gas was carefully removed in vacuum, and the flask with the solution was filled with ethylene (1.1 bar). The solution was stirred for 1.5–2 h at 90 °C in ethylene atmosphere. At following cooling polymerization was initiated. The solution was stirred for 15 min and the ethylene was removed in

**Figure 1.**

Graphical presentation for the influence of water on the ethylene polymerization by complex **9**, activated by 10 equivalents of *i*-Bu<sub>2</sub>AlH together with different equivalents of H<sub>2</sub>O (content of Table 3).

**Table 4.**

Ethylene Polymerization by complexes **9**, **10** and **13**, activated by 100 equivalents of *i*-Bu<sub>2</sub>AlH or 1000 equivalents of MAO

Complexes	Activity in kg polyethylene/ (mol · h) <sup>[a]</sup>	
	Complex +100 <i>i</i> -Bu <sub>2</sub> AlH	Complex +1000 MAO
<i>rac</i> -(EBTHI)ZrF <sub>2</sub> ( <b>9</b> )	0	82
<i>rac</i> -(EBTHI)ZrCl <sub>2</sub> ( <b>10</b> )	0	91
<i>rac</i> -(EBTHI)ZrMe <sub>2</sub> ( <b>13</b> )	0	120

<sup>[a]</sup> 1.1 bar, 1 h; 40 °C; 0.042 mmol of complexes, in 20 mL of toluene

vacuum. The polymer was filtered, washed with toluene and dried in vacuo.

#### Activation by 10 Equivalents of *i*-Bu<sub>2</sub>AlH

*i*-Bu<sub>2</sub>AlH (0.4 ml of a 1.0 M solution, 0.4 mmol) in 19.6 mL was added to complex **1–5** or **7** (0.04 mmol) in 20 mL of toluene under argon. Argon was carefully removed in vacuum, and the flask with the solution was filled with ethylene (1.1 bar). The solution was stirred for 15 min at 40 °C. After 15 min the ethylene was removed. The polymer was filtered, washed with toluene and dried in vacuo.

#### Activation by 10 equiv of *i*-Bu<sub>2</sub>AlH and 5 Equivalents of H<sub>2</sub>O

*i*-Bu<sub>2</sub>AlH (0.4 ml of a 1.0 M solution, 0.4 mmol) and distilled water (3.6 μl, 0.2 mmol) was added to complex **1–5** or **7** (0.04 mmol) in 19.6 mL of toluene under argon. Then argon was carefully removed in vacuum, and the flask with the solution was filled with ethylene (1.1 bar). The solution was stirred for 15 min at 40 °C. After 15 min the ethylene was removed. The polymer was filtered, washed with toluene and dried in vacuo.

#### Activation of Complexes by 10 Equivalents of *i*-Bu<sub>2</sub>AlH and 5 equiv of H<sub>2</sub>O

*i*-Bu<sub>2</sub>AlH (0.8 ml of a 1.0 M solution, 0.8 mmol) and was added to complex **8–12** (0.08 mmol) in 19.2 mL of toluene under argon. Then argon was carefully removed in

vacuum, and the flask with the solution was filled with ethylene (1.1 bar). The solution was stirred for 20 min at 40 °C. Subsequently distilled water (7.2 μl, 0.4 mmol) was added to the solution under ethylene. The polymerization started and the solution was stirred for 15 min at 40 °C. Ethylene was removed, the polymer was filtered, washed with toluene and dried in vacuo.

#### Activation of Complexes by 10 Equivalents of *i*-Bu<sub>2</sub>AlH and *n* equiv. of H<sub>2</sub>O

*i*-Bu<sub>2</sub>AlH (0.8 ml of a 1.0 M solution, 0.8 mmol) was added to complex **9** (0.032 g, 0.08 mmol) in 19.2 mL of toluene under argon. Then argon was carefully removed in vacuum, and the flask with the solution was filled with ethylene (1.1 bar). The solution was stirred for 20 min at 40 °C. Subsequently the calculated amount of distilled water was added to the solution under ethylene. The polymerization started and the solution was stirred for 15 min at 40 °C. Ethylene was removed, the polymer was filtered, washed with toluene and dried in vacuo.

#### Activation of Complexes by 1000 Equivalents of MAO

MAO (16.9 mL of a 1.66 M solution, 28.1 mmol) in toluene was added to complex **9, 10** or **13** (0.042 mmol) dissolved in 10 mL of toluene under argon. This mixture was added to MAO (8.4 mL of a 1.66 M solution, 13.9 mmol) in 10 mL of toluene. Then argon was carefully removed in vacuum, and the flask with the solution was filled with ethylene (1.1 bar). The polymerization started and the solution was stirred for 1 h at 40 °C. Ethylene was removed, the polymer was filtered, washed with toluene and dried in vacuo.

**Acknowledgement:** We are grateful to the Deutsche Forschungsgemeinschaft (Research Training Group 1213 and the SPP 1118, Project-Nr RO 1269/6) and the Russian Foundation for Basic Research (Project code 05-03-32515) for support of this work. We thank our technical staff, in particular Petra Bartels and Regina Jesse, for skilled assistance.

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