



# Catalytic dehydrogenation of cyclooctane with titanium, zirconium and hafnium metallocene complexes

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## ARTICLE INFO

### Article history:

Received 21 November 2008  
Received in revised form 28 January 2009  
Accepted 28 January 2009  
Available online 5 February 2009

### Keywords:

CH bond activation  
Homogeneous catalyst  
Heterogeneous catalyst  
Dehydrogenation  
Titanium  
Zirconium

## ABSTRACT

Metallocene complexes in combination with cocatalysts like methylalumoxane (MAO) are not only excellent catalysts for olefin polymerization but also appropriate catalysts for the activation of alkanes in homogeneous (autoclave) and heterogeneous (fixed bed reactor) reactions. The activities of the catalysts depend on the temperature, the cocatalysts, additives, the central metal and the ligand structure. Generally, complexes with low steric demands and MAO as cocatalyst gave the highest activities. The comparison of different  $\pi$ -ligands resulted in the following activity order: cyclopentadienyl > indenyl > fluorenyl. The influence of  $\sigma$ -ligands and  $n$ -donor ligands gave the following activity order:  $-\text{Cl} > -\text{PMe}_3 > -\text{CH}_2\text{Ph} > -(\text{CH}_2)_4\text{CH}_3 > -\text{NPh}_3$ . The activities depended on the nature of the cocatalyst and decreased in the following order: MAO  $\gg$  AlMe<sub>3</sub> > AlEt<sub>3</sub>. The addition of aluminum powder and the Lewis base NPh<sub>3</sub> increased the activity of the Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO catalyst. The Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO/NPh<sub>3</sub> catalyst showed the highest activity in homogeneous reactions with 458 turnovers in 16 h at 300 °C. The Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO/NPh<sub>3</sub>/Si1102 catalyst gave the highest activity in heterogeneous catalysis with 206 turnovers in 5 h at 350 °C. None of the catalysts required a hydrogen acceptor like an external olefin.

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## 1. Introduction

Hydrocarbons represent the ultimate resource for organic feedstocks especially for petrochemistry. Currently hydrocarbons are produced by thermal decomposition (“cracking”) of alkanes available from crude oil. This process, however, usually needs reaction temperatures up to 1000 °C [1] and requires expensive separation and purification methods because a complex mixture of various hydrocarbons is produced. Consequently, a new selective method for alkane production under mild conditions is desirable. The CH activation of an alkane via oxidative addition to a transition metal is one of the most promising approaches to that target. Significant progress has been made in this area during the past years, particularly with late transition metal catalysts, especially rhodium and iridium complexes [2–7]. These metals are rare and consequently expensive. Furthermore, most of the catalytic CH activation reactions reported in the literature proceed via transfer dehydrogenation. This method has the disadvantage that a hydrogen acceptor, like *tert*-butylethylene is necessary [8–12] to scavenge the produced hydrogen and to shift the equilibrium to the right side. This makes this catalysis uneconomic. CH activation reactions without any hydrogen acceptors at mild conditions are hard to find. Therefore, the catalytic dehydrogenation of alkanes

with complexes of cheap metals and without any hydrogen acceptors is most desirable.

The CH activation of alkanes with titanium, zirconium and hafnium metallocene complexes has not been reported in the literature. These complexes have to be activated with a cocatalyst like methylalumoxane (MAO) for olefin polymerisation. There are indications that also alkanes can be activated in this process: besides the oxidative addition of the alkane to the active center, the  $\beta$ -hydrogen elimination is one of the essential steps in the catalytic CH activation of alkanes. Just this reaction is often described as side or chain-termination reaction in olefin polymerisation [13,14]. Also the intramolecular CH activation of metallocene complexes is known in the literature: a good example is the intramolecular CH activation of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ti reported by Bercaw and co-workers in 1978 [15]. Based on that knowledge, metallocene catalysts should be appropriate candidates for the activation of saturated hydrocarbons under comparatively mild reaction conditions.

## 2. Results and discussion

### 2.1. General considerations

It was a big surprise to learn that the “thermal” decomposition of metallocene catalysts provides new catalysts for the CH activation of alkanes. Therefore, screening experiments with different unbridged, bridged and dinuclear metallocene catalysts were

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performed (Scheme 1). The applied metallocene complexes were prepared in our research group [16–26].

The titanium, zirconium and hafnium complexes had to be activated with a cocatalyst in analogy to olefin polymerisation. The classical activator for metallocene catalyst precursors is methylalumoxane (MAO). The activation reaction can proceed in the following manner [27–32] (Scheme 2).

The exact structure of MAO and the reaction progress is still unknown except that MAO works as a methylating agent and then abstracts a methyl anion from the metal to form a cationic 14e<sup>-</sup> species. MAO consists of a variety of linear and cyclic oligomers which exist in a dynamic equilibrium [33–39].

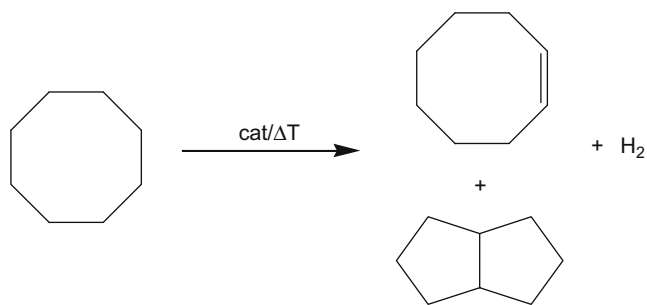
Metallocene catalysts are able to activate alkanes. Therefore, the influences of the cocatalysts, of additives and the lifetimes of catalysts were investigated. The results are summarized in the following chapter.

## 2.2. Homogeneous dehydrogenation of cyclooctane

The titanium, zirconium and hafnium complexes were applied as catalysts for the dehydrogenation of cyclooctane. Due to its comparatively low CH bond energy of 402 kJ/mol [40] and its boiling point of 151 °C, cyclooctane is an appropriate model compound for CH activation experiments.

The activation of cyclooctane with metallocene catalysts gave the CH activation products cyclooctene and bis(3.3.0)cyclooctane along with small amounts of the isomerisation products dimethylcyclohexane, ethylcyclohexane and methylcycloheptane (Scheme 3).

The complexes were dissolved or suspended in cyclooctane and were activated with the respective cocatalyst to form catalysts **1–11** and **16–75**. The addition of triphenylamine to the activated complex gave catalysts **12–15**. The solution was transferred to an autoclave and heated to 300 °C for 16 h. For investigation of the

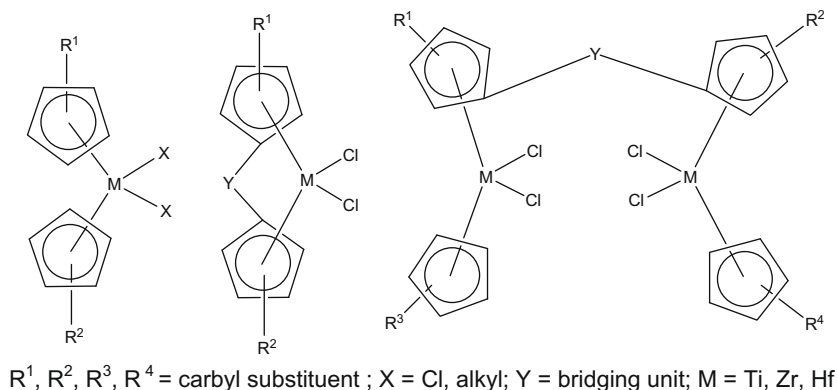


Scheme 3. Dehydrogenation of cyclooctane.

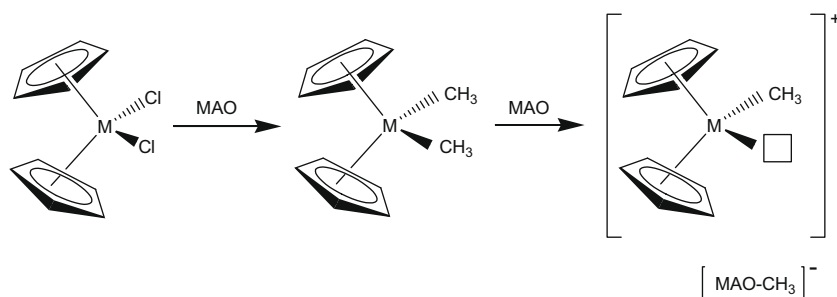
temperature influence, the reaction mixture was heated up to 375 °C. The lifetime of the catalyst Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO (**1**) was investigated in experiments with reaction times up to 72 h. For all experiments, an amount of 0.05–0.07 mmol complex was added to 20 ml of the alkane. A higher amount of complex decreased the activities of the catalysts.

### 2.2.1. Temperature and time dependence of the dehydrogenation of cyclooctane with Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO (**1**)

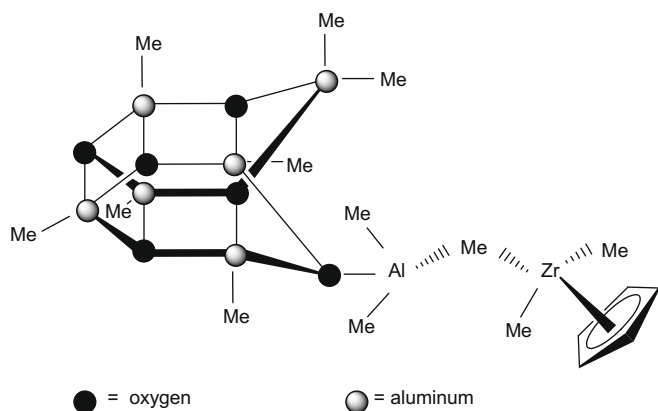
It is evident that most metallocene catalysts do no longer have their original composition at reaction temperatures of 300–400 °C. Nevertheless, the catalyst Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO (**1**) was active for CH activation up to 350 °C: from 200 to 350 °C, a continuous increase of the TON was observed. Simultaneously the isomerisation of cyclooctane increased and the selectivity decreased to 53% at 350 °C. Cracking products were detected neither in solution nor in the gas phase. The results indicate that a new active species is formed by heating the catalyst precursor Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO. The identification of these active species showed that a CpZrMe<sub>2</sub> fragment is incorporated into a six membered MAO cage [41]. Energy calculations and



Scheme 1. General types of tested metallocene complexes.



Scheme 2. Activation of a metallocene complex with MAO.



**Scheme 4.** “Thermally decomposed” metallocene catalyst.

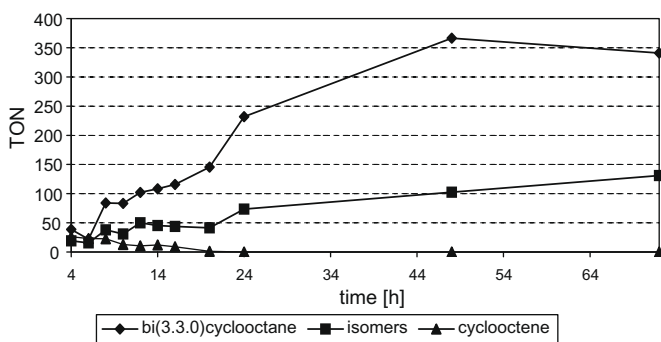
theoretical studies confirm that a Al/O/Me cage is connected over an oxygen atom to such a fragment at temperatures over 300 °C (Scheme 4).

For more simplicity, the organometallic compounds (activated with MAO) will be named as catalysts.

The TON for the CH activation product bi(3.3.0)cyclooctane was 880 at 350 °C. This activity excelled enormously the so far reported catalysts which work without any hydrogen acceptor. The Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO catalyst **1** even showed activities that are of the order of catalysts that need a hydrogen acceptor like *tert*-butylene. The managing of Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO (**1**) without any hydrogen acceptor makes the catalyst more economic.

Besides the temperature resistance of the active species, the lifetime of the catalyst was tested. Therefore, different experiments with reaction times between 4 and 72 h were performed in an autoclave (Scheme 5). Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO (**1**) was used as catalyst for the activation of cyclooctane.

The catalyst was active over a period of 2 d: the TON increased continuously in the period from 4 to 48 h. A further extension of the reaction time achieved no increase of the turnover number



**Scheme 5.** Time dependence of the activation reaction of cyclooctane with Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO (**1**).

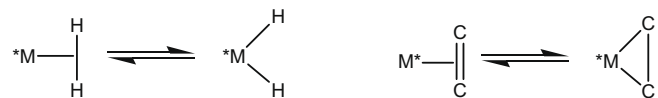
**Table 1**

Activities and selectivities of the catalysts **1** and **9–11**.

Complex	Cocatalyst (Zr:Al)	Al powder (Zr:Al)	No.	TON	Selectivity (CH activation products) (%)
Cp <sub>2</sub> ZrCl <sub>2</sub>	MAO	–	<b>1</b>	181.77*	71
		1:20	<b>10</b>	193.88	81
		1:50	<b>9</b>	200.88	79
		1:100	<b>11</b>	243.84	77

\* Averaged value of 4 experiments.

(Scheme 5). This result can have two reasons: the high temperature could partly destroy the active species and/or the activation products (e.g. H<sub>2</sub>) could block the active species:



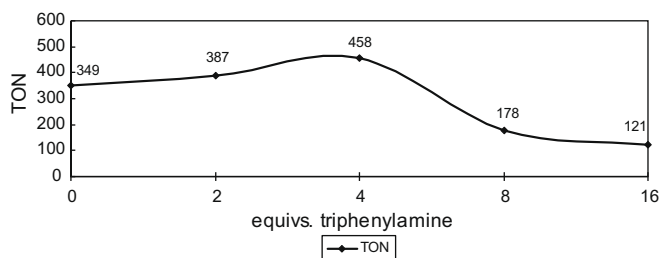
### 2.2.2. Dehydrogenation of cyclooctane with different cocatalysts and additives

Metallocene complexes have to be activated before they can be applied as catalysts for olefin polymerization. When metallocene complexes were used for catalytic CH activation, they were inactive without a cocatalyst like methylalumoxane (MAO). Different from olefin polymerization, CH activation required a clearly lower amount of MAO as cocatalyst: the olefin polymerization needs a metal:Al ratio of 1:2000 and higher, for CH activation experiments, a ratio of metal:Al = 1:50 is sufficient. In contrast to olefin polymerization, an increase of the MAO concentration gave a decrease of the activity in CH activation. Experiments with higher MAO amounts than 1:500 gave an uncatalytic and unselective conversion of cyclooctane by MAO itself.

Since the exact structure of MAO is still unknown, it is complicated to find out structure–efficiency relationships. For that reason, other aluminum containing compounds were investigated as cocatalysts for Cp<sub>2</sub>ZrCl<sub>2</sub>. A comparison of AlEt<sub>3</sub>, AlMe<sub>3</sub> and MAO showed that the activities increased from 39 (AlEt<sub>3</sub>) to 61 (AlMe<sub>3</sub>) and 182 (MAO) turnovers within 16 h. The complex structure of MAO seems to be necessary for high activities: positive surface effects could be responsible for the stabilization of the active species. It is speculated that cluster or cage complexes on the surface of the support material or “nanoclusters” with metals in the oxidation state 0 could play a role in the catalytic cycles. For that reason, aluminum powder and Al<sub>2</sub>O<sub>3</sub> were added to the reaction mixtures of Cp<sub>2</sub>ZrCl<sub>2</sub>/AlMe<sub>3</sub> and Cp<sub>2</sub>ZrCl<sub>2</sub>/AlEt<sub>3</sub>. In the case of AlEt<sub>3</sub> as cocatalyst, no positive effect could be observed. However, the use of AlMe<sub>3</sub>/Al, respectively, AlMe<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> as cocatalysts resulted in an increase of the TONs [41].

Besides the influence of the cocatalyst on the activities, also an influence on the product distributions was evident: AlMe<sub>3</sub> and AlEt<sub>3</sub> containing catalysts produced cyclooctene as main product, while the Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO (**1**) and Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO/Al (**9**) catalysts gave primarily bi(3.3.0)cyclooctane. The highest activity was achieved with the catalyst Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO/Al (**9**). It gave bis(3.3.0)cyclooctane with a total TON of 200. The TON was increased to 244 by raising the amount of aluminum powder (Table 1).

It is known that phosphines can have a positive effect on the activity of iridium containing catalysts [42]. Even if there is the risk that the active center is blocked by a Lewis base and MAO, different amines and phosphines were investigated as additives for Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO catalysts. In the case of zirconium catalysts, no positive effects of Lewis bases were obtained. An exception was NPh<sub>3</sub> (Scheme 6).



**Scheme 6.** Activities of the catalysts **1**, **12**–**15** depending on the amount of additive.

A certain amount of triphenylamine (**13**) increased the activity from 349 (no additive) to 458 (Zr:N = 1:4) turnovers. Higher concentrations of  $\text{NPh}_3$  in the reaction mixture decreased the activity due to an enhanced probability that the Lewis base blocks the active center.

### 2.2.3. Screening of different metallocene complexes as catalysts for the CH activation of cyclooctane

Regarding the structure–efficiency relationships, a multitude of different bridged, unbridged, mononuclear and dinuclear titanium, zirconium and hafnium metallocene complexes were used for the CH activation of cyclooctane.

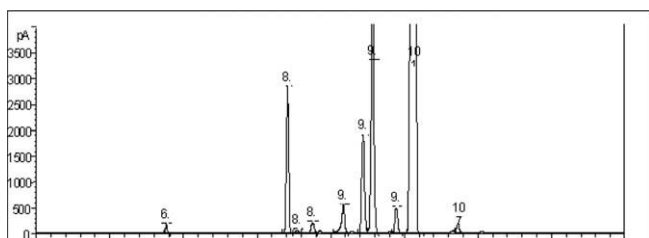
The comparison of analogue titanium, zirconium and hafnium containing catalysts revealed that zirconium is the most suitable central metal for CH activation: the differences of the activities were more conspicuous for the bis(cyclopentadienyl) complexes but both, the cyclopentadienyl and indenyl containing derivatives showed higher activities with zirconium as central metal.

It is obvious that the applied organometallic compound is not identical with the catalytically active species, especially not at higher temperatures. It is not known whether or not all metal atoms of the active compound (picture 1) can contribute as active sites. Nevertheless, a large number of experiments with different mononuclear bridged, unbridged and dinuclear complexes made some trends evident for the structure–efficiency relationship (Tables 2–4):

- Catalysts with cyclopentadienyl ligands gave higher activities than indenyl and fluorenyl containing catalysts.
- An alkyl or a silyl bridge between the  $\pi$ -ligands induced no increase of the activity in spite of the higher stability of such complexes.
- The neighborhood of two metal centers in dinuclear complexes decreased the activities.

Generally, a bulky ligand seems to be disadvantageous for the activity of the catalyst. The structurally simplest metallocene complex  $\text{Cp}_2\text{ZrCl}_2$  activated with MAO (**1**) showed the highest conversion rate of cyclooctane.

The activation of cyclooctane with metallocene catalysts generated different dehydrogenation and isomerisation products. The following scheme represents a typical GC spectrum of the activation of cyclooctane with a metallocene catalyst.



Typical GC spectrum of the dehydrogenation of cyclooctane.

The following products were assigned according to their retention times:

Retention time (min)	Product	Retention time (min)	Product
6.77	THF (cleaning agent)	8.41	Toluene (from MAO)
8.54	<i>cis</i> -Dimethylcyclohexane	8.76	Not identified so far
9.17	Ethylcyclohexane	9.44	Methylcycloheptane
9.57	Bi(3.3.0)cyclooctane	9.9	Cyclooctene
10.13	Cyclooctane	10.73	Decane (impurity)

The following dehydrogenation experiments were performed at 300 °C for 16 h in an autoclave.

The  $\sigma$ -ligands as well as the  $\pi$ -ligands showed an influence on the activities of the catalysts (Table 5): the comparison of dichloride, diphosphine, diamide and dialkyl complexes in combination with MAO as dehydrogenation catalysts gave the following activity order:  $-\text{Cl} > -\text{PMe}_3 > -\text{CH}_2\text{Ph} > -(\text{CH}_2)_4\text{CH}_3 > -\text{NPh}_3$ .

Besides the metallocene complexes, also  $\text{ZrCl}_4$  (**74**) and  $\text{HfCl}_4$  (**75**), activated with MAO, were applied as catalysts for cyclooctane dehydrogenation reactions. Both systems activated cyclooctane:  $\text{ZrCl}_4/\text{MAO}$  (**74**) gave 19.3,  $\text{HfCl}_4/\text{MAO}$  (**75**) 30.7 turnovers. These activities, however, are far behind the activities of metallocene complexes especially those with cyclopentadienyl ligands. This result reinforces the speculation that the ligands have an important influence on the formation of the new active species.

### 2.2.4. CH activation reactions of different alkanes

The activation of linear alkanes is a special challenge due to their higher CH bond energies of 402–427 kJ/mol [43]. Because of their easy availability, industry has a marked interest in the dehydrogenation of linear alkanes.

The catalyst  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  (**1**) was tested for its ability to dehydrogenate different linear, cyclic and branched hydrocarbons. Because of the higher activation energy of these compounds, lower activities were achieved: the alkanes heptane, octane and nonane were transformed with TONs of 3–14 in 16 h at 300 °C. The activation of cyclohexane, cycloheptane and isopentane gave turnover numbers of 11, 25 and 26. In addition, the activation of heptane and octane produced the dimers 2,5-dimethyldodecane and 7-methyl-pentadecane in non-catalytic amounts (Scheme 7).

### 2.3. Heterogeneous dehydrogenation of cyclooctane

For industrial application of catalytic CH activation, the heterogenization of the catalysts is necessary. The reaction conditions of homogeneous and heterogeneous experiments are completely different. Therefore, the results could not be transferred offhand from homogeneous to heterogeneous catalysis. A possible agreement of activity and selectivity had to be tested.

The catalysts were prepared by the “incipient wetness” method. Catalysts **76**–**91** were prepared by supporting selected titanium, zirconium and hafnium containing complexes on the silicagels Davicat<sup>®</sup> SI1102 or SI1700. The support material was heated to 400 °C in an argon stream to remove traces of water. The standard CH activation experiments were performed at 350 °C for 5 h with a WHSV of 2.7. For the investigation of the temperature dependence, the experiments were carried out between 250 and 400 °C.

**Table 2**Activities and selectivities of unbridged mononuclear metallocene catalysts (**1**, **21–38**) (cocatalyst: MAO, Zr:Al = 1:50).

No.	Complex	Products	TON	Selectivity ( $\Sigma$ cyclooctene + bi(3.3.0)cyclooctane) (%)
<b>1</b>		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane cyclooctene	237.39	67
<b>21</b>		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane	180.51	68
<b>22</b>		cis-1,3-Dimethylcyclohexane, ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane cyclooctene	137.15	36
<b>23</b>		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	128.55	71
<b>24</b>		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	96.23	60
<b>25</b>		cis-1,3-Dimethylcyclohexane, ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane	248.47	48
<b>26</b>		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	125.75	69
<b>27</b>		Bi(3.3.0)cyclooctane, cyclooctene	39.64	19

(continued on next page)

Table 2 (continued)

No.	Complex	Products	TON	Selectivity ( $\Sigma$ cyclooctene + bi(3.3.0)cyclooctane) (%)
28		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	62.88	69
29		Bi(3.3.0)cyclooctane	13.89	94
30		cis1,3-Dimethylcyclohexane, ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane	319.73	82
31		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	142.40	63
32		cis1,3-Dimethylcyclohexane, ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane	197.01	79
33		cis1,3-Dimethylcyclohexane, ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	75.82	76
34		cis1,3-Dimethylcyclohexane, ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane	163.36	80
35		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	153.49	79
36		cis1,3-Dimethylcyclohexane, ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane	210.41	79

**Table 2** (continued)

No.	Complex	Products	TON	Selectivity ( $\sum$ cyclooctene + bi(3.3.0)cyclooctane) (%)
37		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	142.83	76
38		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	211.54	77

**Table 3**

Activities and selectivities of mononuclear bridged metallocene catalysts (39–59) (cocatalyst: MAO, Zr:Al = 1:50).

No.	Complex	Products	TON	Selectivity ( $\sum$ cyclooctene + bi(3.3.0)cyclooctane) (%)
39		Methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	18.44	80
40		cis1,3-Dimethylcyclohexane, ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane	207.29	52
41		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	52.03	57
42		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	76.52	59
43		Bi(3.3.0)cyclooctane	2.98	79
44		Methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	65.27	64

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Table 3 (continued)

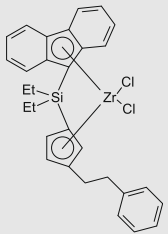
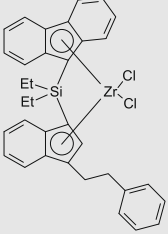
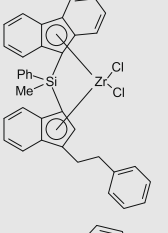
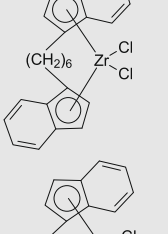
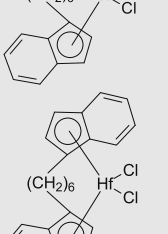
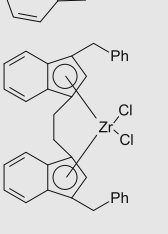
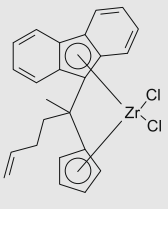

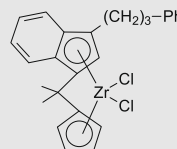
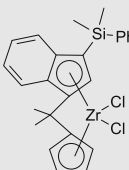
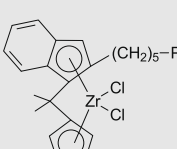
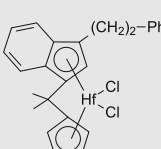
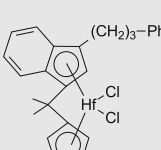
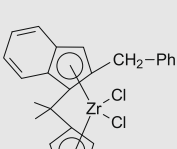
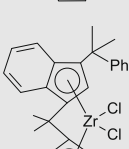
No.	Complex	Products	TON	Selectivity ( $\Sigma$ cyclooctene + bi(3.3.0)cyclooctane) (%)
45		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	59.67	56
46		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	65.55	80
47		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	52.68	44
48		cis1,3-Dimethylcyclohexane, ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane	145.22	79
49		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	28.47	69
50		cis1,3-Dimethylcyclohexane, ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane	24.22	38
51		Bi(3.3.0)cyclooctane, cyclooctene	13.11	71
52		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	105.02	37



Table 3 (continued)

No.	Complex	Products	TON	Selectivity ( $\Sigma$ cyclooctene + bi(3.3.0)cyclooctane) (%)
53		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	148.55	69
54		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	137,90	39
55		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	94.91	68
56		Methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	69.42	86
57		Methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	15.61	52
58		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	139.48	61
59		Methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	37.20	74

The catalysts showed, analogously to the homogeneous catalysts, a clear temperature dependence. The activity of the  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{silicagel}$  (**76**) catalyst increased from 250 to 350 °C (TON = 179 in 5 h). The main product was cyclooctene with a selectivity of 86%. At higher temperatures (400 °C), the activity decreased and bis(3.3.0)cyclooctane was the main product (Table 6).

The catalyst  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SI1102}$  (**76**) gave the CH activation products with selectivities higher than 86% at temperatures up to 350 °C. At 400 °C, the main product was bis(3.3.0)cyclooctane. In a side reaction, cyclooctane was isomerised to give ethylcyclohexane and methylcycloheptane (Scheme 8). In the GC, another product could be detected that has not been identified so far. Because of

its retention time it is assumed that it is a further isomerisation product of cyclooctane.

The comparison of different titanium, zirconium and hafnium containing catalysts gave analogous results compared with the corresponding homogeneous catalysts:

- Zirconium containing catalysts were more active than the titanium and hafnium analogues.
- Cyclopentadienyl ligands showed a positive effect on the formation of the active species.
- The addition of the Lewis base triphenylamine to  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  on SI1102 (**76**) increased the activity from 180 catalytic turnovers to 206.

**Table 4**  
Activities and selectivities of dinuclear zirconium catalysts (**60–64**) (cocatalyst: MAO, Zr:Al = 1:50).

No.	Complex	Products	TON	Selectivity ( $\sum$ cyclooctene + bi(3.3.0)cyclooctane) (%)
<b>60</b>		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane	90.11	84
<b>61</b>		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	83.25	79
<b>62</b>		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	99.40	69
<b>63</b>		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	83.65	79
<b>64</b>		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane	57.08	82

**Table 5**  
Activities and selectivities of metallocene dialkyl, diamide, diphosphine and dichloride catalysts (**65–73**) (cocatalyst: MAO, Zr:Al = 1:50).

No.	Complex	Products	TON	Selectivity ( $\sum$ cyclooctene + bi(3.3.0)cyclooctane) (%)
<b>65</b>		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	237.39	67
<b>66</b>		Methylcycloheptane, bis(3.3.0)cyclooctane, cyclooctene	81.18	59
<b>67</b>		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	46.46	62

Table 5 (continued)

No.	Complex	Products	TON	Selectivity ( $\Sigma$ cyclooctene + bi(3.3.0)cyclooctane) (%)
68		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	107.45	64
69		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	53.03	60
70		Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	156.28	79
71		Methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	31.11	48
72		Methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	90.00	89
73		cis-1,3-Dimethylcyclohexane, ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	198.74	42

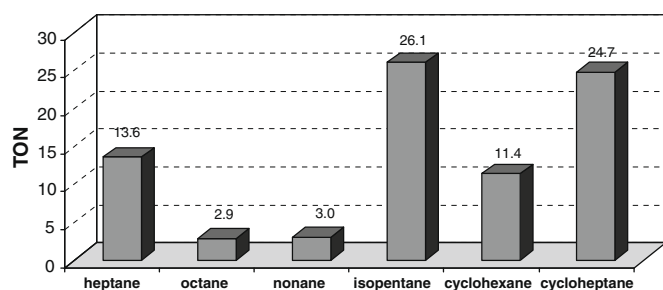
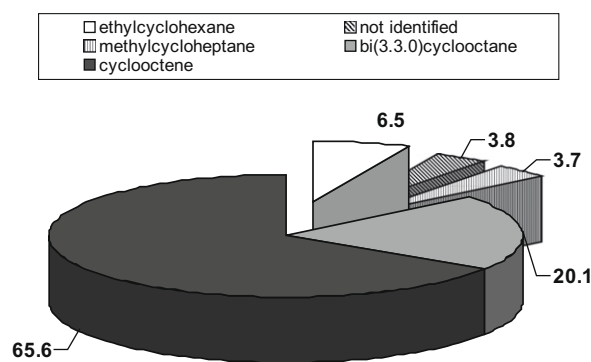
Scheme 7. Activities of  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  (1) for the activation of different alkanes.Scheme 8. Product distribution of the activation of cyclooctane at 350 °C with  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SI1102}$  (76).

Table 6

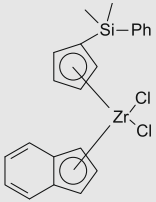
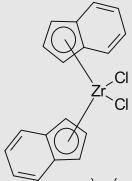
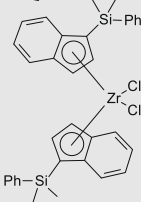
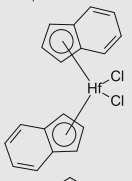
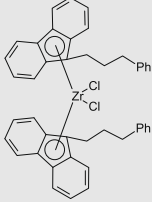
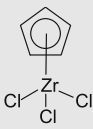
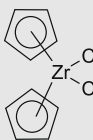
Temperature dependence of the activity of  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}/\text{SI1102}$  (76).

T (°C)	Main product	Average TOF	TON	Selectivity ( $\Sigma$ cyclooctene + bi(3.3.0)cyclooctane) (%)
250	Cyclooctene	2.84	14.70	87
300	Cyclooctene	4.69	23.83	93
350	Cyclooctene	33.20	179.15	86
400	Bis(3.3.0)cyclooctane	3.00	15.24	85

**Table 7**  
Activities and selectivities of the catalysts **77–91** (cocatalyst: MAO, Zr:Al = 1:50).

No.	Complex	Support	Products	TOF (TONs/h)	TON	Selectivity $\Sigma$ cyclooctene + bi-(3.3.0)cyclooctane (%)
77		SI1102	Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	33.20	179.15	65
78		SI1102	Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	4.06	23.50	81
79		SI1700	Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	15.58	97.81	63
80		SI1102	Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	11.98	61.82	51
81		SI1102	Ethylcyclohexane, methylcycloheptane	0.89	4.92	59
82		SI1102	Ethylcyclohexane, cyclooctene	1.35	7.27	76
83		SI1102	Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	1.24	7.36	58
84		SI1102	Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	16.88	85.87	96

Table 7 (continued)

No.	Complex	Support	Products	TOF (TONs/h)	TON	Selectivity $\Sigma$ cyclooctene + bi-(3.3.0)cyclooctane (%)
85		SI1102	Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	8.58	46.67	86
86		SI1102	Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	3.56	17.82	34
87		SI1102	Ethylcyclohexane, cyclooctene	2.06	10.06	80
88		SI1102	Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	0.50	2.86	31
89		SI1102	Ethylcyclohexane	0.54	1.95	60
90		SI1102	Ethylcyclohexane, methylcycloheptane	0.52	1.98	47
91		SI1102	Ethylcyclohexane, methylcycloheptane, bi(3.3.0)cyclooctane, cyclooctene	40.73	206.39	77

Generally, the TONs in the open system (heterogeneous catalysis) were lower than in the closed system (autoclave, homogeneous catalysis) (Table 7).

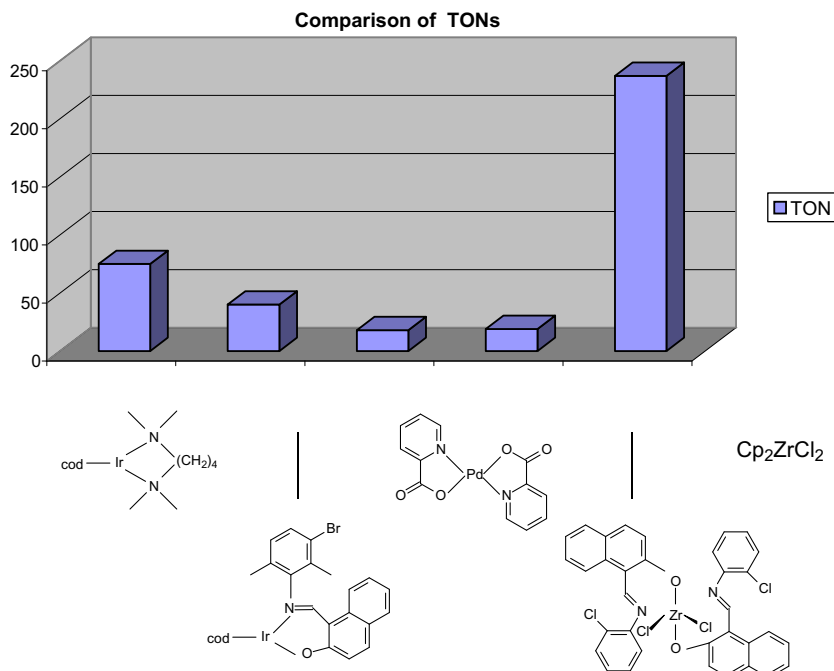
### 3. Summary and conclusions

Metallocene complexes are well known and established catalysts for olefin polymerisation. The big surprise is the fact that they also can be applied for catalytic CH activation reactions. Obviously a new catalytic species is formed at temperatures that are higher than the decomposition temperatures of these complexes. This species is supposed to be a CpZrMe<sub>2</sub> fragment incorporated into

a six membered MAO cage (see [41]). A large number of experiments with different complexes and under different conditions indicated that metallocene complexes are suitable catalysts for the catalytic dehydrogenation of alkanes.

The activation of cyclooctane in the autoclave (homogeneous system) with metallocene catalysts gave other products besides the monoolefin cyclooctene: the catalysts produced the isomerisation products dimethylcyclohexane, ethylcyclohexane, methylcycloheptane and bis(3.3.0)cyclooctane which is generated by CH activation combined with a C<sub>1</sub>–C<sub>5</sub>-bond fusion.

It is evident that the homogeneous catalysts do not have any longer the original homogeneous composition at reaction temper-



**Scheme 9.** Comparison of maximum TONs of the CH activation reaction of cyclooctane and different iridium, palladium and group IV metal complexes.

atures of 300–350 °C. Nevertheless, the activity of Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO increased up to 350 °C. The Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO catalyst converted 50% of cyclooctane into bis(3.3.0)cyclooctane at 350 °C. Thus, the activity of this catalyst is higher than the activity of all published homogeneous catalysts working without hydrogen acceptor. Beyond that, the catalyst had a lifetime of 48 h at 300 °C.

Former results of CH activation reactions of iridium (I) complexes and cyclooctane [44] gave TONs between 10 and 75. For [Ir(cod)LL]X complexes (L = N,N-chelating ligands, amines, phosphines; X = Cl, PF<sub>6</sub>) and cyclooctane TONs up to 40 were obtained [45]. Pd (II) complexes in similar CH activation reactions gave TONs of 18 [46], complexes with group IV metals and N,O chelating ligands of 19 [47]. The highest TON (237) of all CH activation investigations were found for Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO and cyclooctane [41] (Scheme 9).

The cocatalyst influenced the activity and the distribution of the products. The comparison of different aluminum containing cocatalysts with Cp<sub>2</sub>ZrCl<sub>2</sub> gave the following activity order: AlEt<sub>3</sub> < AlMe<sub>3</sub> << MAO. Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO gave bis(3.3.0)cyclooctane as the main product while the corresponding catalysts with AlMe<sub>3</sub> resp. AlEt<sub>3</sub> favored the formation of cyclooctene. The addition of Lewis bases decreased the activity of the catalysts. Triphenylamine made an exception: it increased the activity of Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO by 100 catalytic turnovers.

Regarding the structure-efficiency relationships, a multitude of different bridged, unbridged and dinuclear metallocene complexes was used for the CH activation of cyclooctane. As a result, catalysts with cyclopentadienyl ligands exhibited higher activities than indenyl and fluorenyl containing catalysts. Bridged ligands and neighbored metals in dinuclear complexes decreased the activities. Zirconium catalysts were more active than the homologous titanium and hafnium containing catalysts. The comparison of dichloride, diphosphine, diamide and dialkyl complexes with MAO as dehydrogenation catalysts gave the following activity order: -Cl > -PMe<sub>3</sub> > -CH<sub>2</sub>Ph > -(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub> > -NPh<sub>3</sub>.

For industrial applications of the concept, the heterogenization of the catalysts is necessary. Therefore the respective metallocene/MAO mixture was supported on silcagels and tested for the dehydrogenation of cyclooctane.

The catalysts showed, in analogy to the homogeneous catalysts, a clear temperature dependence. The activity of the Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO/silicagel catalyst increased from 250 to 350 °C (TON = 179 in 5 h). The main product was cyclooctene with a selectivity of 86%. At higher temperatures (400 °C) the activity decreased and bi(3.3.0)cyclooctane was the main product.

The comparison of different titanium, zirconium and hafnium containing catalysts gave analogous results as were obtained for the corresponding homogeneous catalysts: zirconium containing catalysts were more active than the titanium and hafnium analogues. Cyclopentadienyl ligands showed a positive effect on the formation of the active species. The addition of the Lewis base triphenylamine increased the activity of Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO on silicagel from 180 catalytic turnovers to 206.

## 4. Experimental

### 4.1. General considerations

Air- and moisture sensitive reactions were carried out under an atmosphere of purified argon using conventional Schlenk techniques. The products of CH activation experiments were characterized by a GC (Agilent 6890) and GC/MS (FOCUS DSQ™ Thermo Scientific).

### 4.2. Materials

THF, *n*-pentane and methylene dichloride were refluxed over the appropriate drying reagents and distilled under argon. NaH was washed with toluene and pentane before use to remove residual mineral oil. Cyclooctane (COA) was degassed and stored under argon. The organic starting materials were purchased from Aldrich or Arcos and were used without any purification.

### 4.3. Activation of the complexes

The respective metallocene complex was dissolved resp. suspended in the alkane which should be activated. MAO was added

under stirring, a ratio metal (complex) to Al between 1:50 and 1:200 was used. The activation of the complexes was accompanied by a color change.

#### 4.4. Homogeneous dehydrogenation of cyclooctane

An amount of 10–50 mg of the corresponding complex was dissolved or suspended in 20 ml of cyclooctane. The solution was transferred into a laboratory autoclave and was heated to 300–400 °C. After 16 h, the autoclave was cooled on air and the gas as well as the solution were analysed by GC.

#### 4.5. Preparation of the heterogeneous catalysts by “incipient wetness”

First the absorbable amount of the liquid of the support has to be determined. For this purpose, one gram of the support was weighed on a watch glass and the liquid was added dropwise. As soon as there remained a small puddle of visible liquid, the pores of the support are filled. This point is called “incipient wetness”. The required amount of solvent can be calculated via the weight difference. The amount of the liquid depends on the solvent and on the support.

The corresponding complex was dissolved in the calculated amount of toluene and this solution was added slowly to the support material. The solvent was evaporated in a high vacuum. Applying this method, the catalysts **76–91** were prepared.

#### 4.6. Heterogeneous dehydrogenation of cyclooctane

The CH activation experiments were carried out in a stainless steel fixed bed reactor. The standard temperature was 400 °C, the reaction time was 5 h at normal pressure. The WHSV was between 1.1 and 2.7. The samples were taken hourly and identified by GC.

#### Acknowledgment

We thank ConocoPhillips, Bartlesville, USA, for the financial support of the project.

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