“Like Phoenix from the ashes”! Thermally decomposed metalloocene complexes as catalysts for CH activation reactions

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Received on Jan. 21, 2009 Accepted on March 18, 2009

Abstract

Methylalumoxane (MAO) activated metalloocene and amido functionalized ansa half sandwich complexes with group 4 metals are able to activate linear and cyclic alkanes at temperatures in the range of 300-400°C to give the corresponding alkenes, branched isomers and C,C coupling products without a hydrogen acceptor. The new catalytic species are supposed to be MAO cages incorporating metalloocene fragments.

Keywords: CH bond activation; C-C bond coupling; Metalloocene complexes; MAO.

Introduction

Metalloocene and amido functionalized ansa half sandwich complexes with group 4 metals in combination with a cocatalyst like methylalumoxane (MAO) are excellent catalysts for olefin polymerization [1]. Such catalysts have their best performances below 100°C. At higher temperatures, nearly all of them decompose rapidly and lose their catalytic potential for olefin polymerization. Metalloocene complexes of group 4 metals have also been known for their non catalytic potential of CH activation [2-5] as well as other titanium containing complexes [6]. The catalytic functionalization of alkanes under mild conditions is still one of the biggest challenges in research because from all hydrocarbon feedstocks, alkanes are the cheapest class of compounds. Dehydrogenation reactions of alkanes with late transition metal complexes have been described in the literature, especially reactions of various iridium, rhodium and rhenium complexes with alkanes [7-13]. Therefore it was our intention to apply suitable complexes of group 4 metals as catalysts for the activation of alkanes.

Materials and methods

The air and moisture-sensitive reactions were carried out under an atmosphere of purified argon in a hand autoclave. An amount of 10-50 mg of the metalloocene complex was activated with MAO (30% in toluene, M : Al ratio = 1:100). The activated
complex was heated to 300°C for 5 hours. The yellow residue was filtered, washed with THF and pentane and dried in vacuo.

Methylalumoxane (MAO) was purchased from Albemarle (Baton Rouge, USA / Louvain – La Neuve, Belgium). All other starting materials were commercially available and were used without further purification.

The mass spectroscopy was performed with a Varian MAT CH7 instrument at the University of Bayreuth. The GC/MS spectra were obtained with an instrument of THERMO.

Mass spectroscopy

Mass spectra were routinely recorded at the Analytical Center (Zentrale Analytik) of the University of Bayreuth with a VARIAN MAT CH-7 instrument (direct inlet, EI, E = 70 eV) and a VARIAN MAT 8500 spectrometer. Post-processing and data analyses were performed using the software “Maspec II Data system”.

GS/MS

GC/MS spectra were recorded with a Focus DSQ instrument of Thermo. Helium (4.6) was applied as carrier gas. Technical data and temperature programs were used as followed:

- Column flow: 200 ml/min
- Split ratio: 200:1
- Type of the column: TR-5MS (5% phenyl(poly)phenylene-siloxane)
- Length of the column: 30 m; (0.25 μm)
- Temperature program:
  - Start phase: 2 min at 50°C
  - Heating phase: 10°C/min
  - Plateau phase: 15 min at 290°C
- Total running time: 41 min

Gas Chromatography

For the analysis of the organic compounds and the reaction gas of the CH activation reactions, a gas chromatograph 6890 of Agilent was used. Argon (5.0) was the carrier gas.

Technical data and temperature programs used were as follows:

Investigation of the liquid phases:

- Detector: Flame ionization detector
- Column flow: 150 ml/min
- Split ratio: 50:1
- Type of the column: HP-5 (5% phenyl methyl siloxane)
- Length of the column: 30 m; (1.5 μm)
- Temperature program:
  - Start phase: 6 min at 35°C
  - Heating phase: 20°C/min
  - Plateau phase: 2 min at 200°C
- Total running time: 16.25 min
Investigation of the gas phase:

<table>
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**CH activation experiments**

An amount of 20 ml of the degassed cyclooctane was added to 10-50 mg of the metallocene complex and activated with 30% MAO in toluene (ratio M : Al = 1:50 or 1:100) in a hand autoclave. The reaction mixture was heated to 300°C and stirred over 4-72 hours. The reaction mixture was filtered over silica gel. The products of the experiments were characterized by a GC (Agilent 6890) and GC/MS (Focus DSQ Thermo).

**Results and discussion**

The big surprise is that the “decomposition reactions” of metallocene catalysts at 300°C result in defined products that are able to activate linear and cyclic alkanes in a catalytic manner to give the corresponding olefins, branched isomers or C,C coupling products.

The insoluble yellow product formed from the “decomposition reaction” of Cp₂ZrCl₂/MAO (Zr : Al = 1 : 100) at 300°C was characterized by mass spectroscopy, solid state NMR spectroscopy and elemental analysis. The results suggest a mixture of [AlOMe]₆ cages and MAO cages incorporating CpZrMe₂ units. Such a product (A) showed the following mass spectrum.

![Mass spectrum](image)

**Figure 1**: Mass spectrum of the thermally decomposed Cp₂ZrCl₂/MAO (A) (EI = 70eV).
The peak $M^+$ at $m/z = 548$ indicates that the active species could be a 
CpZrMe$_2$ fragment added to a [AlOMe]$_6$ unit formed from MAO. Fragmentation peaks 
at $m/z = 393$ (M-ZrCp), 309 (M - 2Al/2CH$_3$), 264 (M -3 CH$_3$) and 179 (M- 2Al/2CH$_3$) 
confirm this assumption.

The solid state $^{13}$C NMR spectrum (Figure 2) shows an intense signal at $\delta = 32.8$ 
ppm and a shoulder at $\delta = 31.5$ ppm.

![Solid state $^{13}$C NMR spectrum](image)

**Figure 2:** Solid state $^{13}$C NMR spectrum of the decomposed Cp$_2$ZrCl$_2$/MAO.

Further signals appear at $\delta = 113.0, 72.4, 50.7, 25.9,$ and $-7.1$ ppm.

The signal at $\delta = 113.0$ ppm is designated to the Cp ligand$^{[12]}$. Small signals at 
$\delta = 72.4, 50.7$ and $–7.1$ ppm can also be observed when pure MAO is heated to 
$300^\circ C$. These signals could be due to CH$_3$ groups coordinated to Al atoms. The 
significant signal at $\delta = 32.8$ ppm indicates Zr-CH$_3$ groups$^{[14,15]}$. The signal at $\delta = -7.2$ 
ppm is typical for Al-CH$_3$ groups of MAO$^{[16]}$. In the solid state $^{27}$Al NMR spectrum of A, 
the coordination mode (tetrahedral, octahedral) of the Al atoms ($\delta = 3 - 90$ ppm) is 
confirmed$^{[17]}$. The elemental analysis$^{[18]}$ indicates also that a CpZrMe$_2$ fragment is 
incorporated into a six membered MAO cage.

48
Theoretical studies and energy calculations confirm that a six membered (MeAl)O cage structure is supposed to be formed and connected over an oxygen atom to a CpZrMe₂ fragment under these conditions \[^{19,20}\]. When Cp₂ZrMe₂ is heated over 200°C in vacuo, no decomposition could be observed \[^{21}\]. This fact supports the “survival potential” of CpZrMe₂ units at higher temperatures. Only the combination of the metallocene and the aluminum containing components give such a catalyst. The single components do not produce catalytic species for CH activation reactions at higher temperatures.

For the catalytic activation of alkanes, cyclooctane was chosen as the most promising candidate due to its comparatively low CH bond energy of 402 kJ/mol \[^{22}\] and its boiling point of 151°C. Cyclooctane is an appropriate model compound for CH activation experiments.

The activation of cyclooctane with A at 350°C converted 50% of the educt into the products cyclooctene and bi(3.3.0)cyclooctane, along with small amounts of the isomerisation products dimethylcyclohexane, ethylcyclohexane and methylcycloheptane (Figure 4). These products were detected and identified by GC/MS and NMR techniques. In the case of the commercially available products, the retention times of the synthesized products and the commercial products were compared. The presence of a hydrogen acceptor (“sacrificing olefin”) was not necessary. The lifetime of the catalyst was 72 hours.
In spite of the difficult activation of the CH bond of linear alkanes it was also possible to activate them with Cp₂ZrCl₂/MAO (A). At 300°C the TONs ranged between 2.9 (n-octane) and 13.6 (n-heptane). The branched alkane isopentane gave a significant higher TON (26.1) than the linear alkanes (Figure 5).

At a temperature of 350°C the TON of n-octane could be increased to 25.

It is interesting to see that the new catalytically active species is formed at temperatures that are higher than the decomposition temperatures of the parent complex.
Figure 6: Temperature dependence of the activation of cyclooctane with Cp₂ZrCl₂/MAO.

The TON/temperature diagram (Figure 6) shows a strong increase of catalyst activity at temperatures higher than 300°C indicating the formation of the new catalytic species with higher activity than the previous one.

So far, expensive iridium catalysts showed the best performances in CH activation [23-26] reactions. Now, comparatively cheap metal complexes of titanium or zirconium offer a much more attractive access to the catalytic functionalization of alkanes [27].

A large number of experiments with different complexes and under different conditions showed that not only metallocene complexes but also amido functionalized ansa halfsandwich complexes of the type Cp´(SiMe₂)NtBuMCl₂ (Cp´ = unsubstituted or substituted cyclopentadienyl; unsubstituted or substituted indenyl; M = Ti, Zr, Hf) are suitable catalyst components for the catalytic dehydrogenation of alkanes.

Also the type and the concentration of the cocatalyst influenced the activity and the distribution of the products. MAO ratios of 1:1500 (M:Al; M = Ti, Zr, Hf) and higher are most commonly used for the activation of the metallocene complexes in ethylene polymerization [28]. In contrast to this high excess of MAO in polymerization reactions, in these CH activation reactions MAO concentrations of 1:50 (M:Al; M= Ti,Zr,Hf) are sufficient.
The comparison of different aluminum containing cocatalysts with \( \text{Cp}_2\text{ZrCl}_2 \) gave the following activity order: \( \text{AlEt}_3 < \text{AlMe}_3 << \text{MAO} \). \( \text{Cp}_2\text{ZrCl}_2/\text{MAO} \) gave \( \text{bi}(3.3.0)\text{cyclooctane} \) as formation. Additives like amines or phosphanes as well as solid support materials like silica or zeolites can the main product while the corresponding catalysts with \( \text{AlMe}_3 \) and \( \text{AlEt}_3 \) favored cyclooctene increase the activity of such catalysts considerably. But also the nature of the original metalloocene complex plays a role.

The addition of Lewis bases decreased the activity of the catalysts. Triphenylamine made an exception: it increased the activity of \( \text{Cp}_2\text{ZrCl}_2/\text{MAO} \) by 100 catalytic turnovers.

Regarding the structure-efficiency relationship, a multitude of different bridged, unbridged and binuclear metalloocene complexes was used for the CH activation of cyclooctane \[^{[27]}\] .
Figure 8: Activities and selectivities of the metalloene/MAO catalysts.

As a result, catalysts with cyclopentadienyl ligands exhibited higher activities than indenyl and fluorenyl containing catalysts. This is in contrast to the activity trend in catalytic olefin polymerization. Bridged ligands and neighboured metals as in dinuclear complexes decreased the activities. Zirconium catalysts were more active than the homologous titanium and hafnium containing catalysts. The reason for this behavior could be a reduced incorporation of the corresponding metallocene fragments into the MAO cages.

The comparison of Cp2MR2 complexes (R = chloride, phosphane, amide, alkyl) in combination with MAO as dehydrogenation catalysts gave the following activity order:

-Cl > -PMe3 > -CH2Ph > -(CH2)4CH3 > -NPh3.

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

The catalysts showed, in analogy to the homogeneous catalysts, a clear temperature dependence. The activity of the Cp2ZrCl2/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 bis(3.3.0)cyclooctane was the main product.

Conclusions

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 Cp₂ZrCl₂/MAO on silicagel from 180 catalytic turnovers to 206.

Various support materials and additives have an influence on the activity and the product selectivity as well.

Acknowledgements

We thank ConocoPhillips (USA, Oklahoma) for the financial support.

References

[18] Elemental analysis calculated for C₁₄ H₃₂ O₆ Al₈ Zr: C: 30,59; H: 5,88; O: 17,47; Al: 29,46; Zr: 16,60%. Found: C: 33,2; H: 6,0; O: 24,2; Al: 32,0; Zr: 2,5%.