Catalytic thermal and photo-induced CH and CC activation reactions of alkanes with ansa amido functionalized half-sandwich complexes and methylalumoxane ☆

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ABSTRACT

In the literature most of the dehydrogenation reactions of alkanes are described as CH activation reactions of cyclooctane. The best results of CH activation reactions have been found for the reaction of MAO activated metallocene complexes and cyclooctane at temperatures over 300 °C.

The application of ansa amido functionalized half sandwich compounds of the type Ind′Si(Me)2Nt-BuMCl2 (Ind′= monosubstituted indenyl); M = Ti, Zr, Hf) for CH and CC activation reactions is completely unknown in the literature.

In contrast to the dehydrogenation reactions of cyclooctane and the metallocene complexes of the group 4 metals, where the zirconocene complexes give higher TONs than the titanocene complexes the ansa amido functionalized titanium complexes give more than two times higher TONs than the corresponding Zr or Hf complexes. The ansa amido functionalized ligand increases the TONs for the Ti complexes and decreases the TONs of the Zr complexes.

In contrast to the metallocene complexes, the ansa amido functionalized dichloride complexes of Ti show also a higher activity than the corresponding Zr complexes. It is known that the photolysis of organometallic titanium, zirconium and hafnium (IV) compounds can give M(III) radicals. The formation of the active Ti metal centre is easier than in the case of the corresponding Zr and Hf metal compounds.

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1. Introduction

The cheap and abounding but nearly chemical inert alkanes offer a huge potential for the synthesis of sophisticated products. The possibility to convert aliphatic CH bonds into other functional groups offers a wide application of alkanes and the resulting alkenes.

Presently, alkenes are produced by unselective thermal cracking processes [1].

Another possibility to activate inert alkanes can be accomplished by catalytic dehydrogenation reactions.

Late transition metal complexes of iridium [2–8] and palladium [9] gave good results as catalysts for CH activation reactions of alkanes. In the literature most of the dehydrogenation reactions of alkanes are described as CH activation reactions of cyclooctane [10–14]. The best results of CH activation reactions have been found for the reaction of MAO activated metallocene complexes and cyclooctane at temperatures over 300 °C [15,16].

The application of ansa amido functionalized half-sandwich compounds of the type Ind′Si(Me)$_2$N^{t}BuMCl$_2$ (Ind′ = monosubstituted indenyl; M = Ti, Zr, Hf) for CH and CC activation reactions is completely unknown in the literature.

Ansa amido functionalized half-sandwich complexes of titanium are commercially used as homogeneous catalysts for ethylene polymerization reactions at temperatures over 130 °C in high boiling solvents [17] and give polymers with interesting properties like high molecular weights and broad or bimodal molecular weight distributions [18]. At temperatures over 200 °C decomposition of these complexes occurs within a very short time. "Decomposition reactions" of metallocene complexes in the presence of MAO at temperatures over 250 °C indicate the formation of a new product [19] that is able to activate linear and cyclic alkanes.

Therefore it is worthwhile to test half-sandwich complexes for catalytic CH activation reactions under various conditions.

2. Results and discussion

### 2.1. Preparation of the complexes 1–28

The ansa amido functionalized indenyl complexes of titanium, zirconium and hafnium dichloride were synthesized by the reaction of the corresponding ligand precursor system TiCl$_3$∗THF, ZrCl$_4$ or HfCl$_4$.

The substitution of the indenyl group is performed by a lithiation reaction of indene [20] followed by the reaction with the corresponding alkyl, alkenyl or phenyl bromide [21].

The addition of the silyl group to the functionalized indenyl ligand is conducted with n-butyl lithium and the aquimolar amount of the corresponding chloro silyl compound. The reaction of the
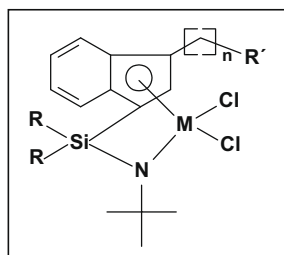
1 - 24
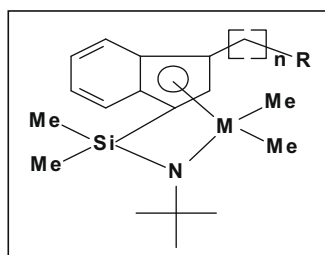
25 M = Zr, n = 0, R = H
26 M = Zr, n = 2, R = Ph
27 M = Hf, n = 0, R = H
28 M = Hf, n = 2, R = Ph

Complex	n	M	R	R`
1	0	Ti	Me	H
2	2	Ti	Me	Ph
3	3	Ti	Me	Ph
4	4	Ti	Me	Ph
5	2	Ti	Me	$CH=CH_2$
6	3	Ti	Me	$CH=CH_2$
7	4	Ti	Me	$CH=CH_2$
8	4	Ti	Ph	Me
9	0	Zr	Me	H
10	2	Zr	Me	Ph
11	3	Zr	Me	Ph
12	4	Zr	Me	Ph
13	2	Zr	Me	$CH=CH_2$
14	3	Zr	Me	$CH=CH_2$
15	4	Zr	Me	$CH=CH_2$
16	4	Zr	Ph	Me
17	0	Hf	Me	H
18	2	Hf	Me	Ph
19	3	Hf	Me	Ph
20	4	Hf	Me	Ph
21	2	Hf	Me	$CH=CH_2$
22	3	Hf	Me	$CH=CH_2$
23	4	Hf	Me	$CH=CH_2$
24	4	Hf	Ph	Me

Fig. 1. Applied ansa amido functionalized complexes **1**–**28**.

indenyl chloro silyl compound with $^tBuNH_2$ in methylene chloride gives the corresponding amino substituted indene derivative [22].

The synthesis of the corresponding zirconium and hafnium complexes proceeds in the conventional manner [23].

Ansa amido functionalized titanium complexes were synthesized by the reaction of $TiCl_3*3THF$ and the corresponding compound, while $PbCl_2$ was added as a mild oxidation agent [24,25] (Fig. 1).

The four tested dimethyl complexes **25–28** of Zr and Hf were synthesized by the reaction of the corresponding dichloride complex and 2 equiv. of MeLi at 0 °C.

2.2. Dehydrogenation reactions of cyclooctane

The ansa amido functionalized catalyst precursors **1–28** were investigated for their catalytic CH activation potential. MAO was used as an activator.

Cyclooctane is an ideal compound for CH activation reactions due to its low dehyrogenation energy [26]. Dehydrogenation experiments are mostly described with this alkane in the literature [27,28].

The catalytic activation reaction of cyclooctane with the complexes **1–28**/MAO gave the isomerization product ethylcyclohexane, the olefin cyclooctene, hydrogen and the CC coupling product bi(3.3.0.)cyclooctane and hydrogen (Scheme 1).

2.2.1. Photochemical CH activation reactions of cyclooctane with the complexes 1, 2, 9, 10, 17, 18, 25 and 27

The MAO activated dichloride complexes **1**, **2**, **9**, **10**, **17** and **18** and the dimethyl complexes **25** and **27** (M:Al ratio 1:100) were dissolved in cyclooctane and the solution was irradiated for 16 h with UV light ($\lambda > 300$ nm) at room temperature. For these reactions it is not necessary to use hydrogen acceptors like *tert*-butylethylene in order to shift the equilibrium to the right side.

The results are given in Table 1.

In all CH activation reactions, the formation of the main product cyclooctene could be detected by GC/MS. The isomerisation product ethylcyclohexane was found with a selectivity of about 20% in all conducted reactions.
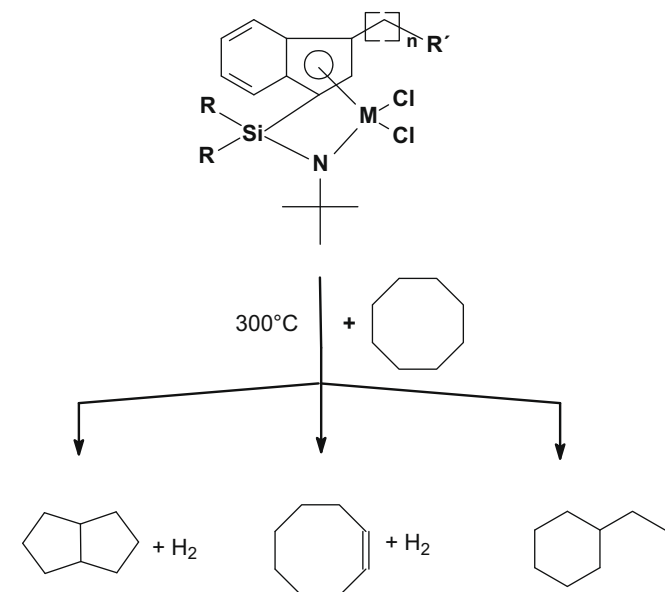
Table 1
TON numbers of the photo - induced reactions of cyclooctane with the MAO activated complexes **1**, **2**, **9**, **10**, **17**, **18**, **25** and **27** at room temperature.
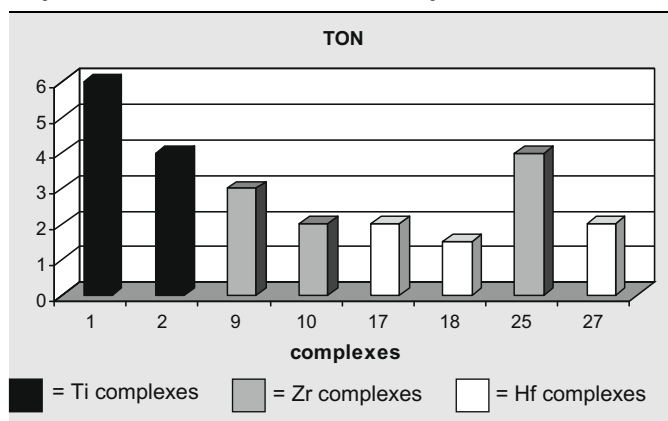
With TONs of 4 and 6 the titanium complexes **1** and **2** showed the highest conversion rates for cyclooctane, adequate to the ansa amido functionalized dimethyl zirconium complex **25** (TON 4).

No difference of the TONs was found for the hafnium dimethyl (**27**) and dichloride complexes (**17**).

The phenyl substituted indenyl complexes gave in all cases lower TONs than the unsubstituted derivatives. The dimethyl complexes of zirconium (**25**) gave higher TONs than the corresponding dichloride complexes.

A positive effect on the formation of cyclooctene was also observed for the unsubstituted complexes **1**, **9** and **25**.

2.2.2. Thermal CH activation reactions of cyclooctane with complexes 1–28

The MAO activated half-sandwich complexes (M:Al ratio 1:100) were heated to 300 °C. At this temperature they formed a new active species. Mass spectroscopy and elemental analysis suggest an analogous product that has been identified from the reaction of Cp_2ZrCl_2 and MAO: An MAO cage with an incorporated CpZrMe fragment [16,19]. The hydrolysis of this species at room temperature produces butenylindene and methane. These results confirm the results of the reaction of MAO and the metallocene complexes of Zr at 300 °C [16,19], where the organic ligand is still connected to the metal at this high temperatures and plays an important role for the activity of the CH activation reactions.

Reactions of cyclooctane and the catalyst precursors at temperatures lower than 200 °C gave no CH activation products.

2.2.3. Comparison of the dichloride and dimethyl complexes of titanium, zirconium and hafnium (1, 9, 17, 24 and 25–28) in catalytic thermal CH activation reactions

To investigate the effect of the two methyl groups instead of the chloride ligands, the activated complexes **1**, **9**, **17**, **24**, **25–28** were reacted with cyclooctane in a handautoclave at various temperatures from 200 °C to 320 °C. The CH activation process is an endothermic reaction and higher temperatures should give higher conversion rates but also lower selectivities of the products (Table 2).
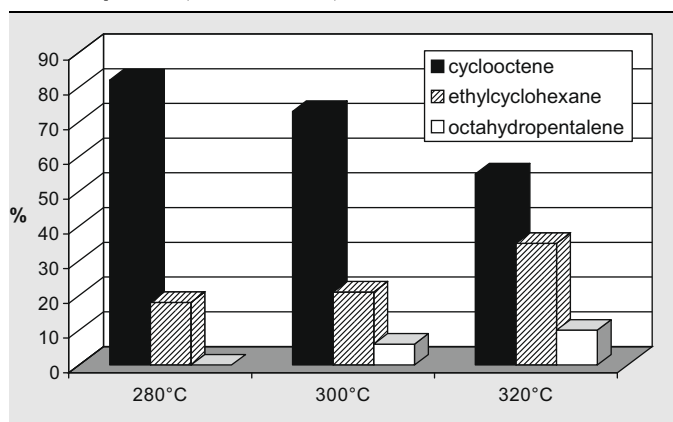
There was no reaction at temperatures below 250 °C. The highest TONs were found at the highest temperature 320 °C. The zirconium dichloride complexes **9** and **10** show higher TONs than the corresponding Hf complexes **17** and **18**. The dimethyl complexes **24–28** gave in all cases higher TON than the corresponding dichloride complexes. The highest TON was found for the dimethyl zirconium complex **25** with a TON of 27. Lower temperatures gave lower TONs. The increase of the temperature from 280 °C to

Scheme 1. Reaction pathway of the activated complexes (M:Al, 1:100) **1–24** and cyclooctane at 300 °C.

Table 2

TONs of the reaction of the complexes **9**, **10**, **17**, **18** and **25–28** and cyclooctane at various temperatures.
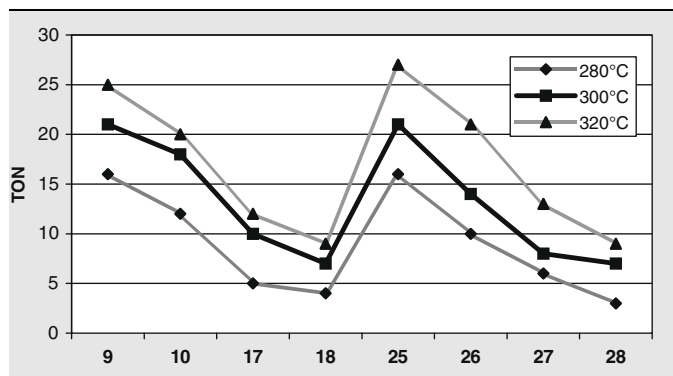
Table 3

Selectivities of the reaction products of the zirconium complex **9** and cyclooctane at various temperatures (reaction time: 5 h).

Table 4

TONs of the reaction of cyclooctane and the complexes **2–4**, **10–12** and **18–20** at 300 °C.
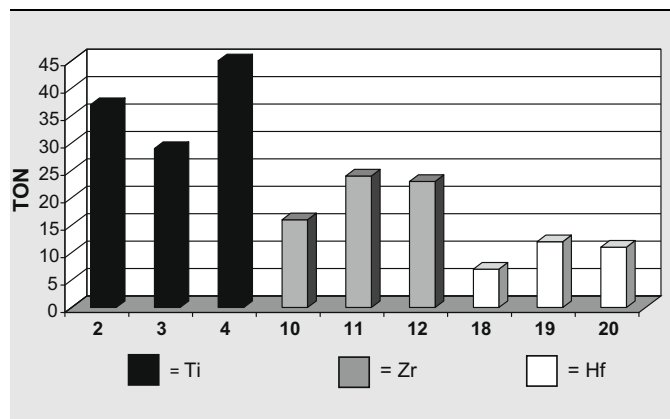
Table 5

TONs of the reaction of cyclooctane and the activated complexes **4**, **7**, **12**, **15**, **20** and **23**.

Complex	TON
4	45
7	22
12	23
15	8
20	11
23	4

320 °C tripled the TON for the Hf complex **28**. The dimethyl complexes of zirconium (**25 and 26**) and hafnium (**27 and 28**) showed no significantly higher TONs than the corresponding dichloride complexes **9**, **10** and **17**, **18** at various temperatures.

The highest selectivities were found at lower temperatures. When cyclooctane was activated with **9**/MAO at 280 °C, the selectivity for cyclooctene was 82%, at 300 °C 73% and at 320 °C 55% when cyclooctane was activated with **9**/MAO. The other applied complexes gave a similar product distribution.

For the reaction of the metallocene complexes of Ti, Zr and Hf and cyclooctane, no cyclooctene was found at temperatures over 280 °C [16,19]. In contrast, the ansa amido functionalized complexes **9**, **10**, **17**, **18**, **25–28** gave also cyclooctene at higher temperatures. The higher the temperature and the longer the reaction time the higher was the amount of octahydropentalene and ethylcyclohexane. At 320 °C, 10% selectivity of octahydropentalene and 35% of the isomerization product ethylcyclohexane were found (Table 3).

2.2.4. Effect of the CH₂ chain length of the indenyl phenyl substituent complexes 2–4, 10–12 and 18–20

The effect of different chain lengths at the indenyl ligand showed no significant influence on the TONs and the selectivities of the products. The highest TON (45) showed complex **4** with Ti as the centre metal and four CH_2 spacers. The lowest TON (7) was found for the corresponding Hf complex **18** with two CH_2 spacer groups. No trend was found for the TONs and the length

of the chain. The number of the CH_2 spacer groups had an effect on the TONs but a trend was not obvious (Table 4).

The Ti complexes **2**– **4** show the highest TON, followed by the Zr complexes **10–12**. The lowest TONs were found for the Hf complexes **18–20**.

2.2.5. Influence of the indenyl substituent R′ (Ph, CH⋯CH₂) of the complexes 4, 7, 12, 15, 20 and 23 (n = 4) on the catalyst activity

The influence of the substituents on the indenyl ligand precursor with a constant spacer length of the CH_2 group ($n = 4$) was investigated. The end groups varied between a phenyl and an ω-alkenyl group.

The positive effect of the phenyl group is shown in Table 5. In contrast to the small ω-alkenyl group –CH_2⋯CH_2, the bulky Ph group is able to increase the TON. The influence of the substituent is so remarkable that the zirconium (**12**) and hafnium (**20**) complexes show nearly three times higher TON than the corresponding ω-alkenyl complexes (Table 5). This behaviour suggests that the active species still contains the bulky substituent.

The influence of the ligand is so drastic that TONs – more than 10 times higher – could be found for the same metals under the same conditions.

3. Summary and conclusion

In contrast to the dehydrogenation reactions of cyclooctane and the metallocene complexes of the group 4 metals, where the zirconocene complexes give higher TONs than the titanocene complexes [16,19] the ansa amido functionalized titanium complexes give more than two times higher TONs than the corresponding Zr or Hf complexes. The ansa amido functionalized ligand increases the TONs for the Ti complexes and decreases the TONs of the Zr complexes.

Table 6
The TONs of the photo-induced reaction of complexes **1**, **2**, **9**, **10**, **24**, **25** and **27** and cyclooctane.
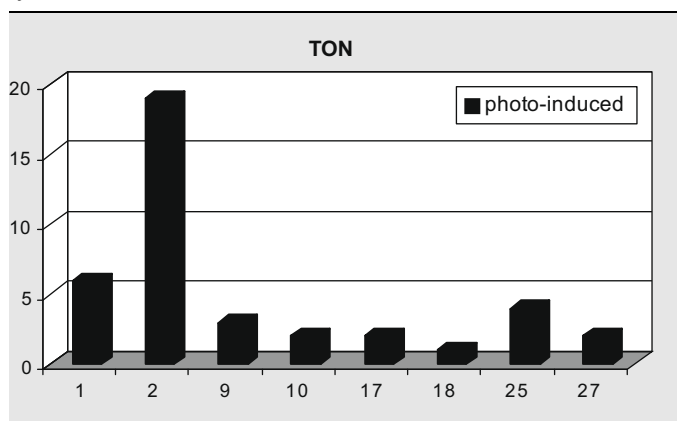
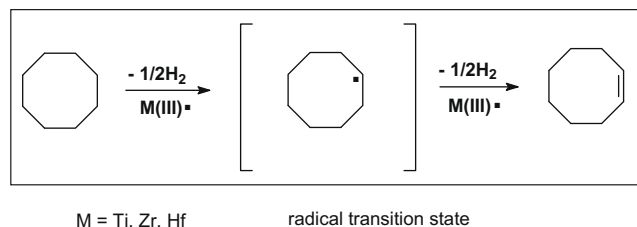**Scheme 3.** Catalytic reaction pathway of an active metal centre and an olefin.

In contrast to the metallocene complexes, the ansa amido functionalized dichloride complexes of Ti show also a higher activity than the corresponding Zr complexes. It is known that the photolysis of organometallic titanium, zirconium and hafnium (IV) compounds can give M(III) radicals [29–31]. The formation of the active Ti metal centre is easier than in the case of the corresponding Zr and Hf metal compounds. The reactions of the Zr and Hf complexes 9, **10**, **17**, **18**, 25 and 27 and cyclooctane proceed with lower TONs than those of the corresponding Ti complexes **1** and **2**. Therefore, the photolysis of the MAO activated ansa amido complexes seems to be initiated by a radical reaction. The elimination of methane and hydrogen was observed, that may indicate the formation of a low valent complex in the first stage of the CH activation reaction similar to the photolysis reaction of Cp_2TiMe_2 [31,32]. In the presence of cyclooctane, the complexes **1, 2, 9, 10, 17, 18, 25** and **27** could transfer a radical from the metal M (III) to the cyclooctane to give cyclooctene and hydrogen (Scheme 2). Low TONs (see Table 6) of the photo-induced reactions of complexes **1, 9, 17, 24, 25** and **27** and cyclooctane confirm this assumption.

Further reaction products, like octahydropentalene – found at the thermolysis reactions – could not be observed. These results support the mechanism of a radically induced catalytic reaction (Scheme 2).
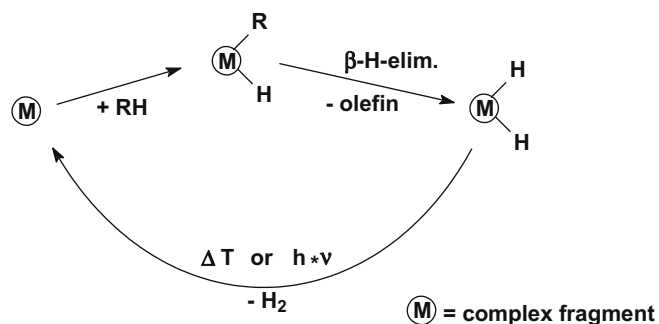
For the thermally activated complexes, the hydrogen substituted dimethyl Zr complex 25 (TON 25) showed the highest TON of the zirconium complexes. The highest TON at all (45) was observed for the titanium containing complexes **4** and **8**.

Intramolecular non catalytic CH activation reactions at 120 °C are known of several substituted cyclopentadienyl complexes of Zr [33,34].

In our case it seems that the formation of the decomposition products depends on the structure of the ligand and the metal. It could be possible that metals of group 4 and the Al from the MAO form the active species at these high temperatures. The key step for CH activation reactions is the formation of an electronically and coordinatively unsaturated species to enable the oxidative addition of the alkane to the metal center. The requirement for this oxidative addition is a low electron density at the metal. Acceptors, which are able to remove the CH bonding electrons and to initiate an electrophile addition reaction are $AlCl_3$ [35], H_2SO_4, HF and super acids [36–38].

Metal surfaces, radicals, carbene and low valent metal complexes are able to act as an acceptor as well as a donor. The combination of the acceptor and donor properties can be very useful [27]. The decomposition products of the group 4 metal complexes **1–33** seem to be subcompounds, this means metal rich compounds. In the GC of the gaseous organic decomposition products methane, CO, NO and C_2H_4 could be found. We assume that these products are formed because of a low oxidation level of the metal centre and a low valence electron concentration. The structure of the active centre depends on the kind of the ligand. Often these compounds show unexpected physical and chemical behaviour (Scheme 3).

The β-hydrogen elimination step can be induced thermally or photochemically to produce the olefin and hydrogen in a catalytic cycle. Thermally activated compounds are able to form the CH activation product cyclooctene and furthermore the CC coupling compound octahydropentalene.

4. Experimental

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 corresponding half-sandwich complex was activated with MAO (30% in toluene, ratio M:Al 1:100). The activated complex was heated to 300 °C for 5 h. The yellow residue was filtered, washed with THF and pentane and dried in vacuo.

Methylalumoxane was purchased from Albemarle (Baton Rouge, USA/Louvain, La Neuve, Belgium). All other starting materials were commercially available and were used without further purification. THF, n-pentane and methylene dichloride were refluxed over the appropriate drying agents and distilled under argon. Cyclooctane was degassed and stored under argon. The organic starting materials were purchased from Aldrich or Acros and used without purification.

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

4.1. Mass spectroscopy

Mass spectra were routinely recorded at the 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[32] Data system".

Scheme 2. CH activation reaction of cyclooctane and M(III) radicals formed from the ansa amido functionalized metal complexes.

4.2. GS/MS

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

Column flow	200 ml/min
Split ratio	200:1
Type of the column	TR-5MS (5% phenyl(equiv.) polysilphenylene–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

4.3. Gas chromatography

For the analysis of the organic compounds and the reaction gas of the CH activation reactions the gas chromatograph 6890 of the agilent company was used. Argon (5.0) was used as carrier gas.

Technical data and temperature programs were used as followed:

Investigation of the liquid phases

Detector	Flame ionisation 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

Detector	Heat conductivity detector
Column flow	30.9 ml/min
Split ratio	10:1
Type of the column	HP-Plot Q (Ethan, Ethen, a.s.o.)
Length of the column	30 m (1.5 μm)
	HP-MOLSIV (for N_2, O_2, CO, H_2, CH_4 a.s.o.) Length of the column: 15 m (25 μm)
Temperature program	Start phase: 6 min at 35 °C
Heating phase	12 °C/min

Plateau phase	1 min at 180 °C
Total running time	19

4.4. Preparation of the dialkyl ansa amido complexes *1 – 25*

The preparation of the corresponding dichloride complexes was performed according to the literature [11,12].

4.5. Preparation of the dialkyl ansa amido complexes *25–33*

In 30 ml of toluene 1.5 mmol of the ansa amido complexes **1–33** was dissolved. Corresponding Grignard bromide (3 mmol) was added and stirred overnight. After filtration of the solution over sodium sulfate, the solvent was evaporated. The residue was washed with 70 ml of pentane and the solvent evaporated. The yields were 45–55%.

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