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Catalytic dehydrogenation of cyclooctane in homogeneous solution with titanium, zirconium and hafnium complexes containing N,O-chelating ligands

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ABSTRACT

A series of new titanium, zirconium and hafnium complexes with the heteroatom chelating ligands hydroxyquinolines, hydroxypyridines and hydroxyimines were synthesized. The complexes were activated with MAO and successfully tested for the catalytic CH activation reactions of cyclooctane. They gave TONs of 1.7–18.7 (300 °C, 16 h) in homogeneous solution. The TONs were clearly influenced by the ligand structure. The endothermic CH activation reaction with group 4 metal catalysts is preferably carried out at higher reaction temperatures (300–400 °C).

1. Introduction

The activation and functionalisation of CH bonds of saturated hydrocarbons is an intensively studied area of research. Currently, the industrial production of organic chemicals is largely based on alkenes which are produced by thermal cracking processes of alkanes [1]. This process is unselective and requires an expensive separation of the products. Consequently, a new selective method for alkene production under mild conditions is desirable. The CH activation of alkanes via oxidative addition to transition metal complexes is one of the most promising approaches to that target. Significant progress has been made in this area during the past several years, particularly with late transition metal catalysts [2–8]. Generally, dehydrogenation reactions were carried out with metal complexes of rhodium [9] and iridium [10]. Currently, the benchmark in homogeneous CH activation of cyclooctane amount to more than 1000 turnovers per 30 min [11]. Like most of the other research groups [12–16], Brookhart et al. activated cyclooctane via transfer dehydrogenation. This method has the big disadvantage that a hydrogen acceptor, like *tert*-butylethylene is necessary to remove the generated hydrogen from the reaction equilibrium. This makes such a reaction inconsiderable for industrial processes. Reports for CH activation of alkanes with organometallic compounds are rare and they describe lower activities than these from transfer dehydrogenation reactions [17].

The catalytic CH activation of alkanes with titanium, zirconium and hafnium complexes is unknown in the literature. These complexes can be activated with a cocatalyst like methylaluminoxane (MAO) and are then excellent catalysts for olefin polymerisation. There are hints that such catalysts are also promising candidates for the activation of saturated hydrocarbons: The oxidative addition of the alkane on the active center and the β-hydrogen elimination of the alkyl ligand are essential steps in the catalytic CH activation of alkanes. The latter reaction is often described as side reaction or chain-termination reaction in the olefin polymerisation process.

2. Results and discussion

2.1. Complex synthesis

The naphthoxyimine ligand precursors were synthesized via a condensation reaction of 2-hydroxy-1-naphthaldehyde and an appropriate aniline [18,19].

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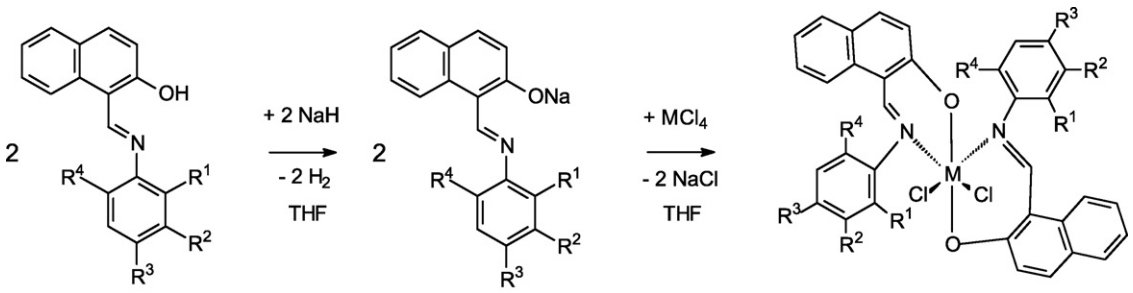
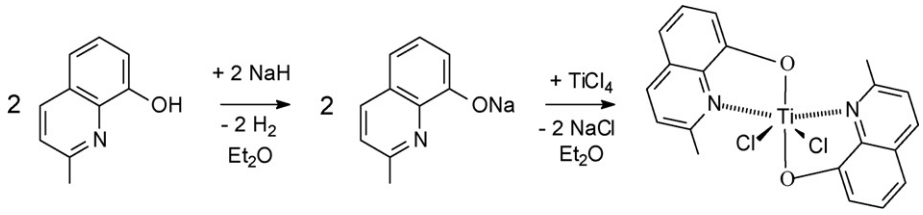
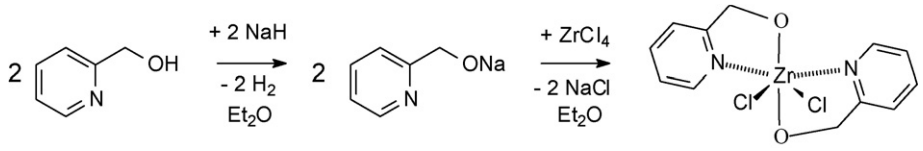


1a M = Ti; R^1, R^2 = H; R^3, R^4 = Cl
1b M = Ti; R^1, R^2 = H; R^3 = Br; R^4 = H
1c M = Ti; R^1, R^2, R^3 = H; R^4 = Cl
1d M = Zr; R^1, R^2, R^3 = H; R^4 = Cl
1e M = Zr; R^1, R^2 = H; R^3, R^4 = Cl
1f M = Zr; R^1, R^2 = H; R^3 = Br; R^4 = H
1g M = Zr; R^1, R^4 = Me; R^2 = H; R^3 = Br
1h M = Zr; R^1, R^2 = Me; R^3, R^4 = H
1i M = Zr; R^1, R^4 = i-propyl; R^2; R^3 = H
1j M = Zr; R^1 = t-butyl; R^2, R^3, R^4 = H
1k M = Zr; R^1, R^4 = Me; R^2, R^3 = H
1l M = Zr; R^1, R^2 = H; R^3 = n-butyl; R^4 = H
1m M = Hf; R^1, R^2, R^3 = H; R^4 = Cl
1n M = Zr; R^1, R^2 = H; R^3, R^4 = Cl

Scheme 1. Synthesis of complexes **1a**–**n**.



Scheme 2. Synthesis of complex **2a**.



Scheme 3. Synthesis of complex **2b**.

The complexes were synthesized from the reaction of the sodium salt of the ligand precursors and the metal tetrachloride. For this purpose, the naphthoxyimine compound and sodium hydride were reacted. A group IV metal chloride was added to the sodium alkoxylate in a ratio of M:L = 1:2. After preparation and workup, the complexes were obtained as yellow solids (Schemes 1–3).

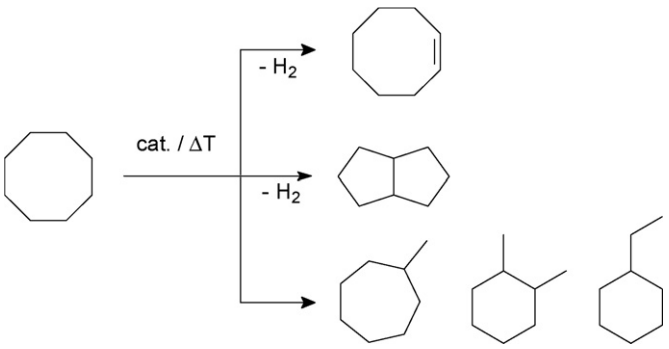
A similar complex type was synthesized by the reaction of 2-methyl-8-hydroxyquinoline and 2-hydroxymethyl-pyridine with NaH followed by the addition of $TiCl_4$ respectively $ZrCl_4$.

Besides bis(2-methyl-8-quinolinato) zirconium dichloride (**2c**) [20], bis(8-quinolinato) titanium dichloride (**2d**) [21] and bis(8-quinolinato) zirconium dichloride (**2e**) [22] were synthesized according to the literature.

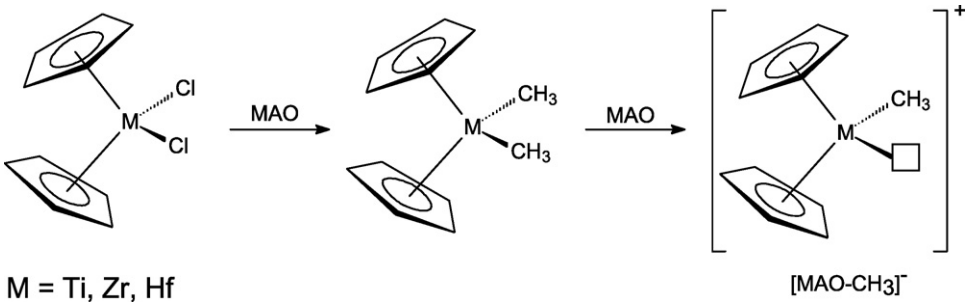
2.2. Homogeneous dehydrogenation of cyclooctane

The titanium, zirconium and hafnium complexes were tested as catalysts for the dehydrogenation of cyclooctane. In a homogeneous catalytic CH activation reaction they converted cyclooctane into cyclooctene and bis(3.3.0)cyclooctane along with small amounts of the isomerisation products dimethylcyclohexane, ethylcyclohexane and methylcycloheptane (Scheme 4).

The titanium, zirconium and hafnium complexes could not be used directly as catalysts for the dehydrogenation of cyclooctane. They needed a cocatalyst like MAO. It can be assumed that the activation step proceeds in an analogous manner (Scheme 5) [23–28]:



Scheme 4. Catalytic reactions of cyclooctane.



Scheme 5. Activation of a metallocene dichloride complex with MAO.

The exact structure of MAO and the reaction progress are still unknown except that MAO works as a methylating agent and then abstracts a methyl anion from the metal to form a cationic species. Besides this, studies proved that MAO consists of a variety of linear and cyclic oligomers which exist in a dynamic equilibrium [29–35].

The complexes **1a**–**n** and **2a**–**e** were dissolved or suspended in cyclooctane and were activated with MAO to form the catalysts **4a**–**n** and **3a**–**e**. The solutions were transferred to an autoclave and heated to 300 °C for 16 h. In order to investigate the temperature influence on the activities and selectivities, the reaction mixtures were heated to 375 °C.

*2.2.1. Dehydrogenation of cyclooctane with N-alcoholate complexes (**3a**–**e**)*

The complexes **1a**–**e** were activated with MAO with a ratio M:Al = 1:50 to form the catalysts **3a**–**e**. The zirconium containing catalysts showed no catalytic dehydrogenation of cyclooctane at 300 °C, the titanium catalysts effected low conversions of cyclooctane to cyclooctene respectively bis(3.3.0)cyclooctane. The activities (given as TONs) and selectivities towards CH activation products are summarized in the following table (Table 1).

The catalytic activities of the zirconium catalysts **3c** and **3e** were furthermore investigated at 350 °C. As the catalysts gave no catalytic dehydrogenation at 300 °C, a remarkable activation of cyclooctane was observed at 350 °C (Scheme 6). This result suggest that the zirconium complex needs higher activation energy than the titanium containing catalysts to catalyse the endothermic CH activation reaction. It is also very likely that only at higher temperatures a new efficient active species is formed. Besides the production of cyclooctene and bis(3.3.0)cyclooctane, the isomerisation of cyclooctane increased at 350 °C, so that the products 1,2-dimethylcyclohexane, ethylcyclohexane and methylcycloheptane were produced. The unidentified product with a TON = 21.82 (**3e**) respectively 6.16 (**3c**) also seems to be an isomerisation product as can be seen from the retention time of the fraction in the GC analysis.

*2.2.2. Dehydrogenation of cyclooctane with imine catalysts of titanium, zirconium and hafnium (**4a**–**n**)*

The complexes **1a**–**n** were activated with MAO to form the catalysts **4a**–**n**. The investigation of the temperature influence gave an analogous result as for catalysts **3c** and **3e**: a higher reaction temperature resulted in higher TONs as it was expected for an endothermic reaction. The higher temperatures, especially 350 and 375 °C, enhanced the isomerisation of cyclooctane so that the selectivity of catalyst **4i** decreased from 60.9 (325 °C) to 48.6 (350 °C) respectively to 27.9 (375 °C).

The influence of the central metal on the catalytic activity was also investigated. The titanium, zirconium and hafnium complexes with monochloro (**4b**, **4d**, **4m**) and dichloro (**4a**, **4e**, **4n**) substituted imine ligands were tested at 300 °C in an autoclave (Scheme 7).

The catalysts with monochloro substituted imine ligands (**4b**, **4d**, **4m**) showed generally higher TONs than catalysts **4a**, **4e** and **4n**. In both cases, the zirconium containing catalyst gave a higher activity than the corresponding titanium and hafnium catalysts. The difference, however, was higher using the monochloro substituted complexes. Besides the higher activity, the zirconium catalysts also achieved higher selectivities towards CH activation products (Scheme 7).

It is evident that most catalysts do not have any longer the original composition at reaction temperatures of 300–375 °C. Nevertheless, the catalysts were active up to 375 °C (Table 2) and the original ligands had a high influence on the activities and selectivities of the actual catalysts (Scheme 8). It is obvious that the ligands are involved in the formation and stabilisation of the new active species.

Catalysts with para-substituted aniline fragments (**4f** and **4l**) gave the lowest dehydrogenation rates for cyclooctane. A substitution in the ortho position increased the TONs. The highest catalytic activity showed the ortho-chloro-substituted catalyst **4d** with a TON of 18.7.

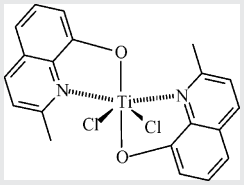
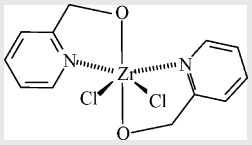
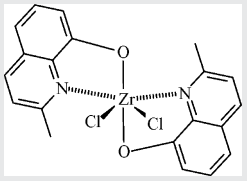
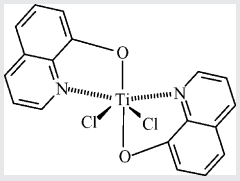
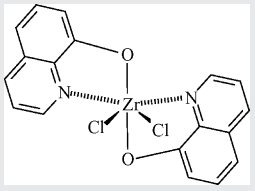
In a similar manner, olefin polymerisation catalysts like Cp_2ZrCl_2/MAO that "decompose" at temperatures above 100 °C are able to activate cyclooctane and other alkanes at higher temperatures but with much better activities (TON = 180, in 5 h, at 300 °C [36]). Preliminary results indicate that in all these cases Zr/Al cages with various substituents are the active species.

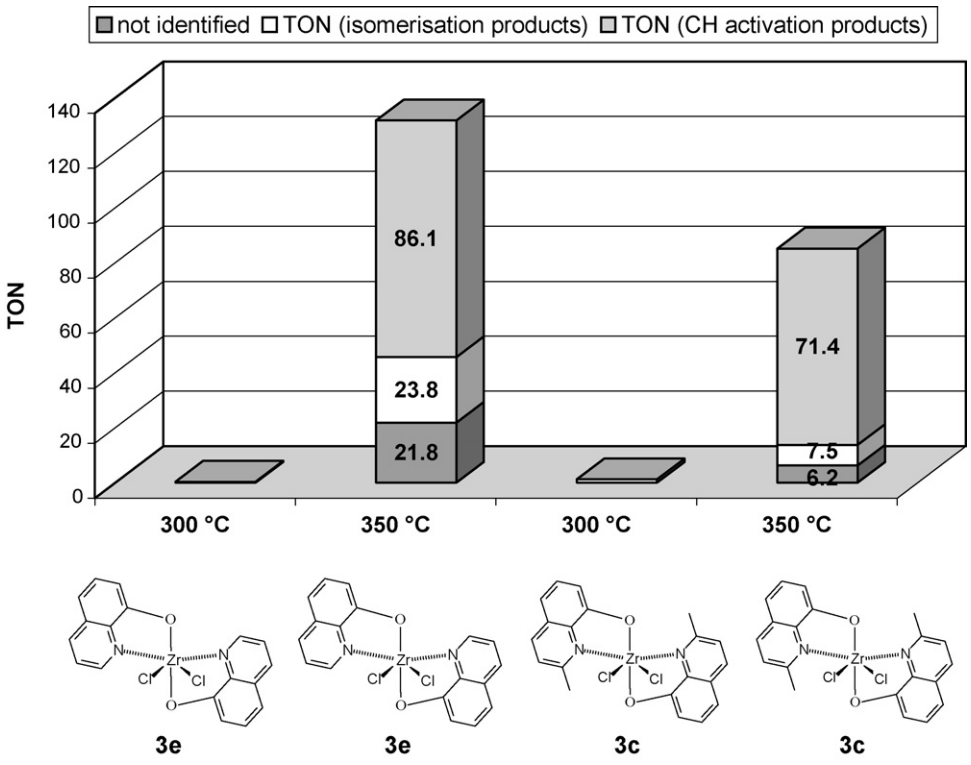
3. Summary and conclusions

The novel titanium, zirconium and hafnium complexes **1a**–**n** and **2a**–**b** containing N,O-chelating ligands were synthesized. As ligand precursors 2-methyl-8-hydroxyquinoline, 2-hydroxymethylpyridine and different naphthoxyimines were applied. The naphthoxyimine ligand precursors can be prepared from relatively inexpensive starting materials.

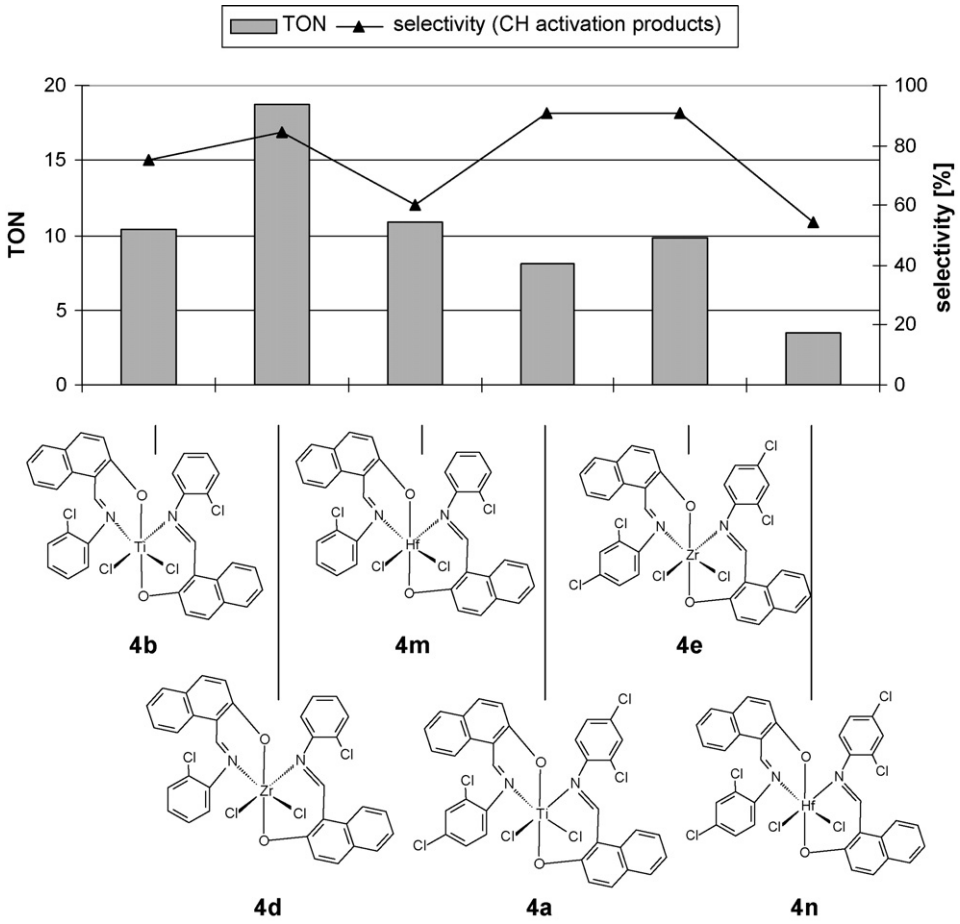
Titanium, zirconium and hafnium complexes as catalysts for the catalytic dehydrogenation of cyclooctane have not been reported in the literature so far. As a consequence, these catalysts can only be compared with the well-known and expensive iridium, rhodium and platinum containing catalysts. The group IV metal catalysts gave lower TONs than the iridium systems (see [37–41]). Nearly all tested catalysts gave a catalytic CH activation of cyclooctane in homogeneous solution. They showed TONs of 1.7–18.7 (300 °C, 16 h) in homogeneous solution. The TON was clearly influenced by the ligand structure: catalysts with a para-substituted aniline fragment (**4f** and **4l**) gave the lowest rates of dehydrogenation of cyclooctane. A substitution in the ortho position increased the TONs. An increase of the temperature increased the activities remarkably: TON (CH activation products) = 86 (**3e**, 350 °C), 71 (**3c**, 350 °C) and 55 (**4i**, 375 °C).

Table 1
Activities and selectivities of catalysts **3a–e**

No.	Complex	Cocatalyst	TON	Selectivity (CH activation products) (%)
3a		MAO	4.3	84.7
3b		MAO	1.7	70.8
3c		MAO	1.9	0.0
3d		MAO	5.1	40.8
3e		MAO	0.7	37.9



Scheme 6. Temperature dependence of the activities of catalysts **2c** and **2e**.



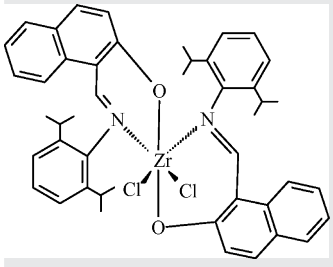
Scheme 7. Influence of the central metal (**4a**, **4b**, **4d**, **4e**, **4m**, **4n**) on the TON and the selectivities towards CH activation products.

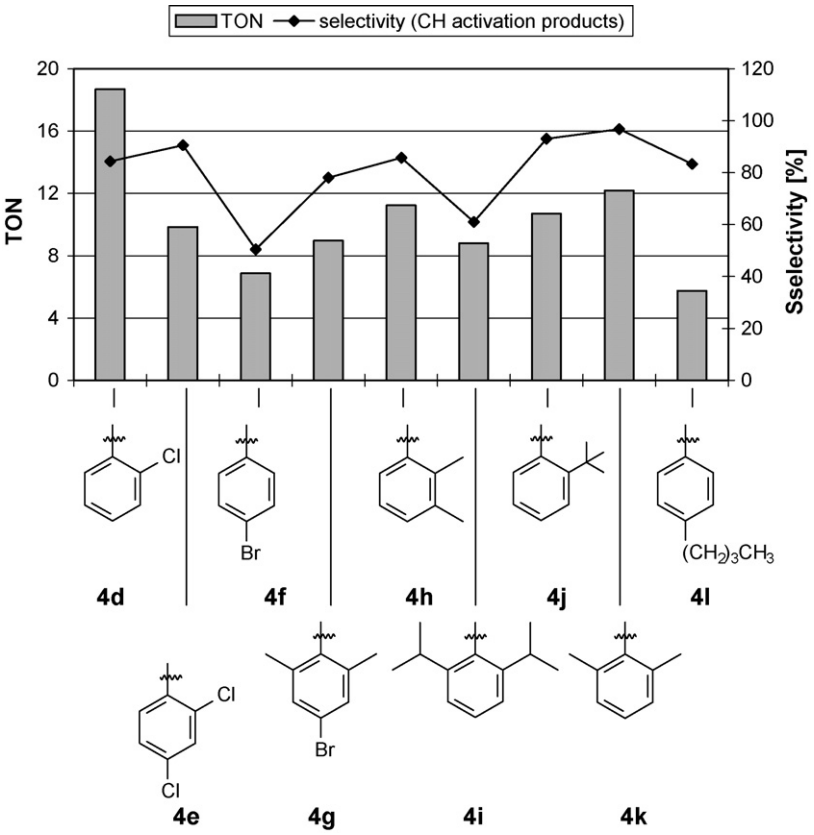
4. Experimental

4.1. General considerations

Air- and moisture-sensitive reactions were carried out under an atmosphere of purified argon using conventional Schlenk techniques. NMR spectra were obtained on a Bruker ARX250 instrument at ambient temperatures (21 °C). ^{1}H NMR spectra were reported in terms of chemical shifts (δ, ppm) relative to the residual solvent peak (5.31 ppm for CD_2Cl_2). The multiplicities were designated as follows: s, singlet; d, doublet; m, multiplet. 13C{1H} NMR spectra were recorded fully decoupled by broad-band decoupling and are reported in terms of chemical shifts (δ, ppm) relative to the solvent peak (53.80 ppm, the center line of a quintet for CD_2Cl_2). Elemental analyses were determined on a VarioEl III instrument. Mass measurements were performed using a VARIAN MAT CH7 instrument (direct inlet, electron impact ionization, 70 eV). The products of CH activation experiments were characterized with a GC (Agilent 6890) and GC/MS (FOCUS DSQ Thermo). For GC measurements a 30 m HP-5 column (film 1.5 μm) was used. The measuring program was: 6 min at 35 °C (starting phase); 20 °C/min (heating phase); 2 min at 200 °C (final phase). The products were detected by a flame ionization detector. For GC/MS measurements a 30 m TR-5MS column was used. The measuring program was 8 min at 35 °C (starting phase); 15 °C/min (heating phase); 2 min at 250 °C (final phase).

Table 2
Temperature dependence of catalyst **4i**/MAO

Complex	Temperature (°C)	TON	Selectivity (%)
	300	9.5	56.8
	325	12.0	60.9
	350	37.7	48.6
	375	97.9	27.9



Scheme 8. Activities and selectivities of catalysts **4d–k**.

4.2. Materials

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

4.3. General procedure for the synthesis of alkoxyimine titanium, zirconium and hafnium complexes

The desired ligand precursor was dissolved in 50 ml of THF and 1 equiv. NaH was added. After the completion of the hydrogen evolution, an amount of 0.5 equivalents of MCl_4 (M = Ti, Zr, Hf) was added, and the solution was stirred for 16 h at room temperature. The solvent was evaporated in vacuo; the residue was suspended in CH_2Cl_2. After filtration over Na_2SO_4, the solvent was evaporated. The residue was washed with 50 ml pentane and dried in vacuo. The complexes were obtained as yellow or orange powders.

(**1a**) From 0.95 g (3 mmol) of 1-[[(2,4-dichlorophenyl)imino] methylenyl]-2-naphthalenol and 0.17 ml (0.28 g, 1.5 mmol) $TiCl_4$ was obtained an amount of 0.43 g (0.57 mmol, 38%) of **1a** as an orange brown powder. NMR data for **1a**: ^{1}H NMR (250 MHz, 21 °C, CD_2Cl_2): 9.47 (s, 2H), 8.19–7.05 (m, 20H). MS data for **1a**: 748 ($M^{\bullet+}$) (9), 713 (100), 677 (8), 434 (52), 314 (58), 263 (31).

(**1b**) From 1.3 g (4 mmol) of 1-[[(4-bromophenyl)imino] methylenyl]-2-naphthalenol and 0.22 ml (0.38 g, 2 mmol) $TiCl_4$ was obtained an amount of 0.79 g (1.02 mmol, 51%) of **1b** as a brown powder. Spectroscopic data for **1b**: ^{1}H NMR (250 MHz, 21 °C, CD_2Cl_2): 8.96 (s, 2H), 8.16–6.53 (m, 20H). MS data for **1b**: 769 ($M^{\bullet+}$) (13), 732 (100), 697 (8), 653 (5), 443 (61), 324 (23).

(**1c**) From 0.56 g (2 mmol) of 1-[[(2-chlorophenyl)imino] methylenyl]-2-naphthalenol and 0.11 ml (0.19 g, 1 mmol) $TiCl_4$ was obtained an amount of 0.38 g (0.56 mmol, 56%) of **1c** as an orange brown powder. MS data for **1c**: 680 ($M^{\bullet+}$) (9), 645 (100), 435 (18), 400 (94), 280 (33).

(**1d**) From 1.13 g (4 mmol) of 1-[[(2-chlorophenyl)imino] methylenyl]-2-naphthalenol and 0.47 g (2 mmol) $ZrCl_4$ was obtained an amount of 0.70 g (0.97 mmol, 48%) of **1d** as an yellow powder. NMR data for **1d**: ^{1}H NMR (250 MHz, 21 °C, CD_2Cl_2): 9.47 (s, 2H), 8.19 (d, 2H), 7.89–7.75 (m, 2H), 7.60–7.38 (m, 8H), 7.25–7.13 (m, 8H). ^{13}C {^{1}H} (62 MHz, 21 °C, CD_2Cl_2): 157.1 (CH), 136.9 (CH), 130.6 (CH), 129.7 (CH), 128.5 (CH), 128.4 (CH), 127.7 (CH), 124.1 (CH), 121.4 (CH), 119.5 (CH), 119.3 (CH). MS data for **1d**: 722 ($M^{\bullet+}$) (30), 687 (41), 442 (56), 281 (100), 246 (53).

(**1e**) From 1.26 g (4 mmol) of 1-[[(2,4-dichlorophenyl)imino] methylenyl]-2-naphthalenol and 0.47 g (2 mmol) $ZrCl_4$ was obtained an amount of 0.83 g (1.05 mmol, 52%) of **1e** as a yellow powder. NMR data for **1e**: ^{1}H NMR (250 MHz, 21 °C, CD_2Cl_2): 9.47 (s, 2H), 8.20 (d, 2H), 7.90–7.77 (m, 2H), 7.61–7.36 (m, 8H), 7.22–7.00 (m, 8H). MS data for **1e**: 792 ($M^{\bullet+}$) (14), 755 (19), 476 (25), 314 (82), 280 (54), 126 (100).

(**1f**) From 0.65 g (2 mmol) of 1-[[(4-bromophenyl)imino] methylenyl]-2-naphthalenol and 0.23 g (1 mmol) $ZrCl_4$ was obtained an amount of 0.32 g (0.39 mmol, 39%) of **1f** as a yellow powder. NMR data for **1f**: ^{1}H NMR (250 MHz, 21 °C, CD_2Cl_2): 9.40 (s, 2H), 8.17–6.55 (m, 20H). MS data for **1f**: 812 ($M^{\bullet+}$) (100), 777 (64), 487 (56), 325 (26).

(**1g**) From 0.71 g (2 mmol) of 1-[[(4-bromo-2,6-dimethylphenyl) imino]methylenyl]-2-naphthalenol and 0.23 g (1 mmol) $ZrCl_4$ was

obtained an amount of 0.27 g (0.31 mmol, 31%) of **1g** as a yellow powder. NMR data for **1g**: ^{1}H NMR (250 MHz, 21 °C, CD_2Cl_2): 9.19 (s, 2H), 8.04–7.03 (m, 16H), 2.24 (s, 12H). MS data for **1g**: 868 ($M^{\bullet+}$) (2), 833 (6), 353 (100), 273 (32).

(**1h**) From 0.83 g (3 mmol) of 1-[[(2,3-dimethylphenyl)imino] methylenyl]-2-naphthalenol and 0.35 g (1.5 mmol) $ZrCl_4$ was obtained an amount of 0.53 g (0.75 mmol, 50%) of **1h** as a yellow powder. NMR data for **1h**: ^{1}H NMR (250 MHz, 21 °C, CD_2Cl_2): 9.32 (s, 2H), 8.16–7.07 (m, 18H), 2.37 (s, 6H), 2.12 (s, 6H). MS data for **1h**: 7108 ($M^{\bullet+}$) (29), 673 (60), 436 (21), 400 (16), 274 (100), 258 (32), 132 (24).

(**1i**) From 0.66 g (2 mmol) of 1-[[(2,6-diisopropylphenyl)imino] methylenyl]-2-naphthalenol and 0.23 g (1 mmol) $ZrCl_4$ was obtained an amount of 0.78 g (0.95 mmol, 95%) of **1i** as a yellow powder. NMR data for **1i**: ^{1}H NMR (250 MHz, 21 °C, $CDCl_3$): 9.13 (s, 2H), 8.06–7.06 (m, 18H), 3.10 (septet, 4H), 1.22 (d, 24H). ^{13}C {^{1}H} (62 MHz, 21 °C, $CDCl_3$): 166.0 (C_q), 162.3 (CH), 144.8 (C_q), 143.0 (CH), 140.0 (C_q), 135.5 (CH), 133.1 (C_q), 130.4 (CH), 130.1 (CH), 129,2 (CH), 128.8 (CH), 127.5 (C_q), 126.0 (CH), 125.1 (CH), 124.4 (CH), 123.4 (CH), 120.7 (CH), 119.0 (CH), 108.5 (C_q), 128.3 (CH), 23.4 (CH_3) (isomers). MS data for **1i**: 823 ($M^{\bullet+}$) (11), 787 (4), 492 (5), 330 (40), 162 (100).

(**1j**) From 0.91 g (3 mmol) of 1-[[(2-*tert*-butylylphenyl)imino] methylenyl]-2-naphthalenol and 0.35 g (1.5 mmol) $ZrCl_4$ was obtained an amount of 0.90 g (1.17 mmol, 78%) of **1j** as a yellow powder. NMR data for **1j**: ^{1}H NMR (250 MHz, 21 °C, $CDCl_3$): 9.28 (s), 9.02 (s), 8.96 (s), 8.21–7.07 (m), 1.46 (s) (isomers). MS data for **1j**: 766 ($M^{\bullet+}$) (18), 731 (20), 464 (7), 302 (100), 281 (29).

(**1k**) From 0.55 g (2 mmol) of 1-[[(2,6-dimethylphenyl)imino] methylenyl]-2-naphthalenol and 0.23 g (1 mmol) $ZrCl_4$ was obtained an amount of 0.36 g (0.50 mmol, 50%) of **1k** as a yellow powder. NMR data for **1k**: ^{1}H NMR (250 MHz, 21 °C, $CDCl_3$): 9.17 (s), 8.96 (s), 8.18 (s), 8.18–7.10 (m), 2.45 (s), 2.28 (s) (isomers). MS data for **1k**: 710 ($M^{\bullet+}$) (52), 673 (100), 436 (29), 400 (21), 274 (53).

(**1l**) From 0.61 g (2 mmol) of 1-[[(4-butylphenyl)imino] methylenyl]-2-naphthalenol and 0.23 g (1 mmol) $ZrCl_4$ was obtained an amount of 0.46 g (0.60 mmol, 60%) of **1l** as a yellow powder. NMR data for **1l**: ^{1}H NMR (250 MHz, 21 °C, $CDCl_3$): 9.37 (s, 2H), 8.14–6.89 (m, 20H), 2,65 (t, 4H), 1,62 (quintett, 4H), 1,45–1,30 (m, 4H), 0.95 (t, 6H). ^{13}C {^{1}H} (62 MHz, 21 °C, $CDCl_3$): 136.1 (CH), 129.5 (CH), 129,2 (CH), 127.9 (CH), 123.4 (CH), 122.2 (CH), 120.2 (CH), 118.9 (CH), 35.1 (CH_2), 33.6 (CH_2), 22.3 (CH_2), 13.7 (CH_3). MS data for **1l**: 766 ($M^{\bullet+}$) (100), 731 (73), 631 (28), 464 (43), 302 (34).

(**1m**) From 1.13 g (4 mmol) of 1-[[(2-chlorophenyl)imino] methylenyl]-2-naphthalenol and 0.64 g (2 mmol) $HfCl_4$ was obtained an amount of 0.56 g (0.69 mmol, 34%) of **1m** as a yellow powder. NMR data for **1m**: ^{1}H NMR (250 MHz, 21 °C, $CDCl_3$): 9.47 (s, 2H), 8.25–7.13 (m, 20H). MS data for **1m**: 810 ($M^{\bullet+}$) (37), 775 (46), 530 (61), 280 (100), 246 (64).

(**1n**) From 1.26 g (4 mmol) of 1-[[(2,4-dimethylphenyl)imino] methylenyl]-2-naphthalenol and 0.64 g (2 mmol) $HfCl_4$ was obtained an amount of 0.88 g (1.00 mmol, 50%) of **1n** as a yellow powder. MS data for **1n**: 880 ($M^{\bullet+}$) (2), 844 (3), 564 (2), 315 (100), 280 (64).

*4.4. Synthesis of the alcoholate titanium and zirconium complexes **2a** and **2b***

An amount of 5 mmol of the respective ligand precursor was dissolved in 50 ml Et_2O and 0.12 g (5 mmol) NaH was added at 0 °C. After completed hydrogen evolution, an amount of 2.5 mmol MCl_4 (M = Ti, Zr) was added and the solution was stirred for 24 h at room temperature. The solvent was evaporated in vacuo; the residue was suspended in CH_2Cl_2. After filtration over Na_2SO_4, the solvent was evaporated. The residue was washed with 50 ml pentane and dried in vacuo. The complexes were obtained as yellow powders.

(**2a**) From 0.8 g (5 mmol) 2-methyl-8-hydroxyquinoline and 0.275 ml (0.47 g, 2.5 mmol) $TiCl_4$, an amount of 0.63 g (1.45 mmol, 58%) of **2a** was obtained as a light yellow powder.

MS data for **2a**: 434 ($M^{\bullet+}$) (11), 399 (100), 383 (6), 348 (21), 276 (36), 240 (26).

(**2b**) From 0.55 g (5 mmol) 2-hydroxymethyl-pyridine and 1.17 g (2.5 mmol) $ZrCl_4$, an amount of 0.57 g (1. 5 mmol, 60%) of **2b** was obtained as a light yellow powder. Anal. Calc. for $C_{20}H_{16}Cl_2N_2O_2Ti$ (**2b**) C: 39.82; H: 3.91; N: 7.26. Found: C: 38.09; H: 3.20; N: 7.40. MS data for **2b**: 342 (8), 286 (4), 127 (11), 108 (51).

4.5. Homogeneous dehydrogenation of cyclooctane

An amount of 10–50 mg of the corresponding complex was dissolved or suspended in 20 ml of cyclooctane and activated with MAO (M:Al = 1:50). The solution was transferred into a laboratory autoclave and was heated to 300–400 °C. After 16 h, the autoclave was cooled to room temperature and the gas as well as the solution were analysed by GC.

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