



# Heterogeneous catalysts for the dehydrogenation of saturated hydrocarbons

Silke Taubmann, Helmut G. Alt\*

Laboratorium für Anorganische Chemie, Universität Bayreuth, Universitätsstraße 30, D-95440 Bayreuth, Germany

## ARTICLE INFO

### Article history:

Received 10 January 2008

Received in revised form 22 February 2008

Accepted 22 February 2008

Available online 4 March 2008

### Keywords:

CH bond activation  
Heterogeneous catalyst  
Dehydrogenation  
Iridium complexes  
Fixed bed reactor  
Support materials  
Additives

## ABSTRACT

A series of new heterogeneous iridium containing catalysts was synthesized by the incipient wetness method. The used support materials were SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, and MCM-41. These catalysts are able to dehydrogenate cyclooctane to give cyclooctene and hydrogen without a sacrificing olefin. The catalysts showed TONs up to 1008 in 5 h and selectivities over 90%. The activities, selectivities and stabilities of the catalysts can be increased by addition of suitable support materials and additives. The heterogeneous dehydrogenation reactions showed a high temperature dependence with a temperature maximum depending on the individual coordination compound. The iridium containing catalysts also activated the linear alkanes *n*-pentane and *n*-octane in catalytic CH-activation reactions.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

The selective catalytic activation of chemical bonds remains a challenging and significant goal of modern chemical research. An attractive research area is the transformation of inexpensive hydrocarbon feedstocks into more useful value-added products by low energy processes [1]. In this respect, the catalytic alkane dehydrogenation to give olefins and hydrogen is a key step reaction. The products are valuable intermediates and can be used in various industrial processes like polymerisation, oligomerisation, dimerisation, functionalisation a. o. reactions.

The crucial step of a catalytic CH-activation reaction is the formation of an electronically and coordinatively unsaturated active species. Low valent transition metal species have the potential to insert into an alkane CH bond to give an alkyl metal hydride (oxidative addition of an alkane to a transition metal). A subsequent  $\beta$ -hydrogen elimination reaction produces the olefin and hydrogen [2].

The catalytic dehydrogenation is a very young research area in coordination chemistry. The first report of a stoichiometric dehydrogenation of cyclooctene to cyclooctadiene with an iridium phosphine complex came from Crabtree et al. [3] in 1979. In the early 1980s, examples of oxidative addition reactions of CH bonds to late transition metals were described [4,5]. Baudry et al. [6]

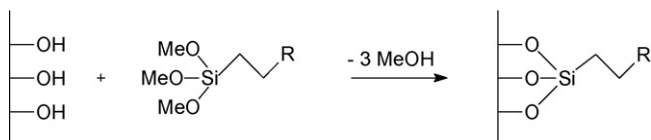
reported a catalytic dehydrogenation reaction of cyclooctane by a rhenium polyhydride complex. This is a transfer dehydrogenation reaction which catalyses the transfer of hydrogen from alkanes to sacrificial olefinic hydrogen acceptors. In the following years, many transfer dehydrogenation reactions were reported in the literature [7–18]. Brookhart et al. used an iridium bis(phosphinite) *p*-XPCP pincer complex which revealed turnover numbers (TONs) >1000 within 30 min [19]. The advantage of such a transfer dehydrogenation reaction is that the hydrogen acceptor eliminates the generated hydrogen shifting the equilibrium to the right side. However, the disadvantage is the hydrogen acceptor because its use makes such a reaction uneconomic. Another way to separate the products from the catalytic center is the performance of a heterogeneous reaction in an open system as in a fixed bed reactor. Therefore, the catalysts have to be heterogenized on appropriate support materials. Heterogeneous dehydrogenation reactions are a promising alternative to transfer dehydrogenation reactions obtaining similar TONs. Such heterogeneous CH-activation reactions were not reported in the literature.

## 2. Results and discussion

### 2.1. General

The coordination compounds [Ir(cod)(PR<sub>3</sub>)<sub>2</sub>]<sub>2</sub>PF<sub>6</sub> (R=Ph, Cy, *o*-Tol, *m*-Tol, *p*-Tol) [20–22], [Ir(cod)(NR<sub>3</sub>)<sub>2</sub>]<sub>2</sub>PF<sub>6</sub> (R=Ph, *p*-Tol, Benz) [23], [Ir(cod)biquin]PF<sub>6</sub> [23], cyclooctadiene iridium pyrazine-2-carboxylate [24], and cyclooctadiene iridium

\* Corresponding author. Tel.: +49 921 55 2555; fax: +49 921 55 2044.  
E-mail address: [helmut.alt@uni-bayreuth.de](mailto:helmut.alt@uni-bayreuth.de) (H.G. Alt).



**Scheme 1.** Synthesis of functionalized support materials (R=PPh<sub>2</sub>, CH<sub>2</sub>NH<sub>2</sub>).



**Scheme 2.** Catalytic dehydrogenation of saturated alkanes.

quinoline-2-carboxylate [24] were synthesized by known procedures.

The novel heterogeneous catalysts were synthesized by supporting different metal complexes on various materials (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, MCM-41, zeolites) by the method of incipient wetness. This impregnation method maximizes the dispersion on the surface. The influence of additives on activities and selectivities for dehydrogenation reactions of cyclooctane were investigated with two different catalyst types. The additives for the various catalysts were added directly during the heterogenisation. Catalysts were also prepared by using a functionalized support material resulting from condensation reactions of hydroxy groups and a substituted methoxysilane [25–33] (Scheme 1).

The prepared catalysts were investigated in a fixed bed reactor for dehydrogenation reactions of linear alkanes (*n*-octane, *n*-pentane) and cycloalkanes (cyclooctane) (Scheme 2).

For the CH-activation reactions, the catalysts were transferred under argon into the reactor tube which was connected with the pipe system of the fixed bed reactor. The reactor tube was heated up to 350–550 °C. The standard reaction temperature was 400 °C. The reaction solutions were analyzed hourly by GC.

The dehydrogenation reactions produced other products besides the monoolefin cyclooctene: The isomerisation products methylcycloheptane, ethylcyclohexane, cis-1,3-dimethylcyclohexane and other dehydrogenation products like 2,4-octadiene, dimethylbenzene and octahydropentalene were obtained. The reactions could be controlled by varying the catalyst parameters (coordination compounds, support materials, additives).

## 2.2. Dehydrogenation activities of different heterogeneous iridium complexes

At high temperatures, obviously most of the organometallic compounds have no longer the original composition. Remarkably, the investigations of structure–efficiency relationships of catalysts showed that the nature of the organic ligands has a relevant impact on the activity and selectivity of the corresponding catalysts. Therefore, different coordination compounds with various heteroatom ligands (phosphines, amines, *N,N*- and *N,O*-chelating ligands) were heterogenized.

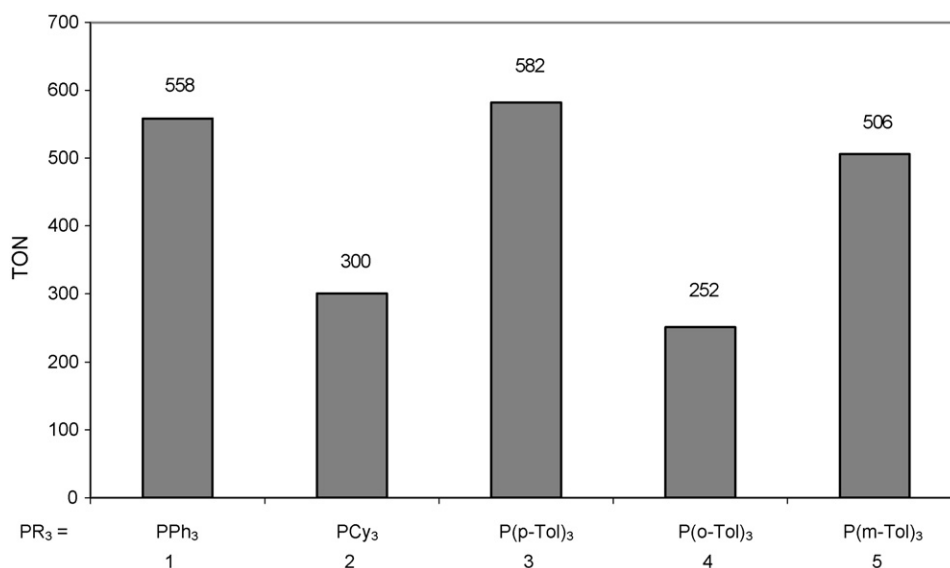
The heterogeneous phosphorus containing catalysts **1–5** converted cyclooctane to cyclooctene with generally high TONs between 252 (**4**) and 582 (**3**) (Fig. 1). The phosphine ligands are supposed to be an essential component of the new active species, formed at higher temperatures. Also, the kind of the phosphine compound influenced the activities which can be observed for the tritoluylphosphine: Catalyst **3** showed the highest TON (582), whereas catalyst **4** achieved only 252 turnovers. Changing the position of the methyl group gave the following range of activities: *ortho* ≪ *meta* < *para*. The heterogeneous [Ir(cod)(PR<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub> catalysts **1–5** showed selectivities between 95.7 and 98.6%.

The catalysts [Ir(cod)(NPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub> (**6**) and [Ir(cod)(Np-Tol<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub> (**7**) are the corresponding amine derivatives of [Ir(cod)(PPh<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub> (**1**) and [Ir(cod)(Pp-Tol<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub> (**3**). In contrast to the phosphine containing catalysts, the amine containing species showed much lower TONs of 29 (**6**) and 19 (**7**). These results make obvious that the phosphine substituents are essential for the activity.

Furthermore, coordination compounds with *N,N*- and *N,O*-chelating ligands were investigated for their catalytic dehydrogenation potential. The catalysts **8–10** dehydrogenated cyclooctane with TONs of 88 (**10**) up to 198 (**9**) (Fig. 2). In contrast to the activities, the catalysts **8–10** exhibited selectivities similar to the phosphine containing catalysts: 99.7 (**8**), 98.7 (**9**) and 95.5% (**10**).

## 2.3. Influence of the weight hourly space velocity (WHSV) on the activities of the dehydrogenation of cyclooctane

The WHSV is defined as follows:  $WHSV = m(\text{alkane})/m(\text{cat})/h$ . A higher WHSV (alkane flow) causes a higher conversion per time unit. This is essential for an industrial application. The upper limit



**Fig. 1.** TONs for cyclooctane activation with the [Ir(cod)(PR<sub>3</sub>)<sub>2</sub>]PF<sub>6</sub> catalysts (R=Ph (**1**), Cy (**2**), *p*-Tol (**3**), *o*-Tol (**4**), *m*-Tol (**5**)) supported on SiO<sub>2</sub> (Davicat® SI1102).

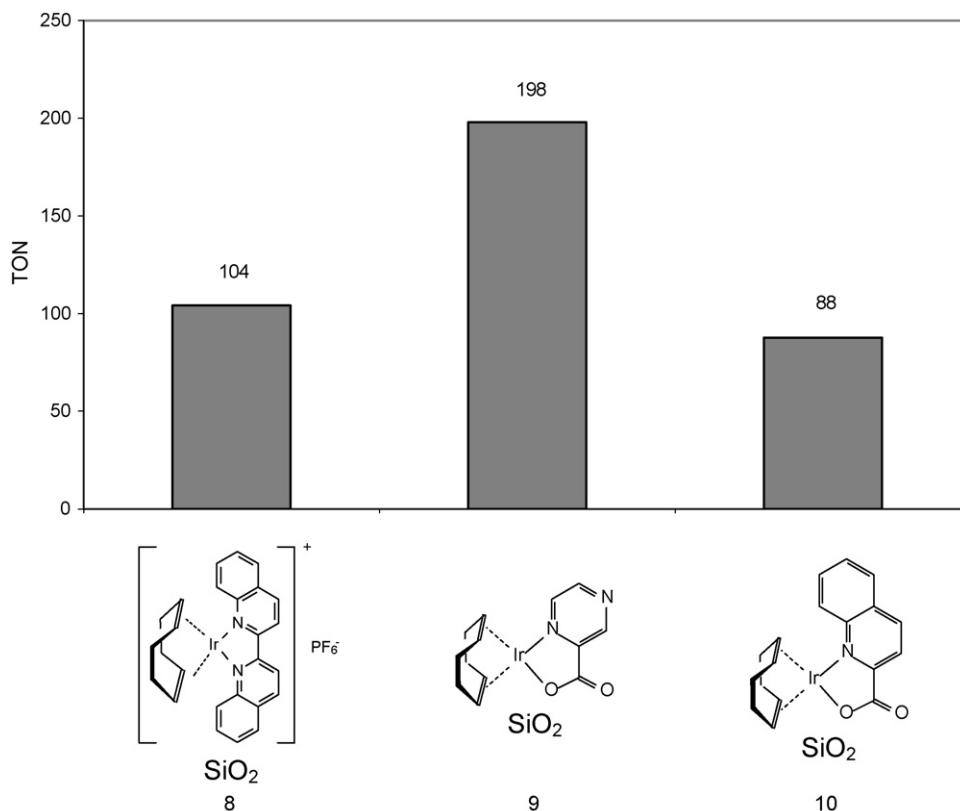


Fig. 2. TONs for cyclooctane activation with the iridium catalysts 8–10 supported on Davicat® SI1102.

is the reaction rate. The alkane needs a certain residence time at the catalyst for a complete reaction. Therefore, catalysts have to be synthesized which work with high WHSVs.

In the literature, only one reference is reported [34]: The heterogeneous  $\text{IrH}(\text{CO})(\text{PPh}_3)_3/\text{SiO}_2$  catalyst converted isopentane to isopentene with WHSVs of 0.9 and 1.9. These WHSV values will be obviously surpassed. Also, the  $\text{IrH}(\text{CO})(\text{PPh}_3)_3$  complex supported on silica was used for dehydrogenation of cyclooctane. This heterogeneous catalyst exhibited TONs of 457 and 435 with very high WHSVs of 2.7 and 5.4 (Fig. 3). The best selectivity (97.9%) was achieved at a WHSV of 5.4.

#### 2.4. Influence of the reaction temperature on the activities of heterogeneous iridium catalysts

The variation of the reaction conditions showed a strong dependence of the TONs on the reaction temperature (Fig. 4). Increasing

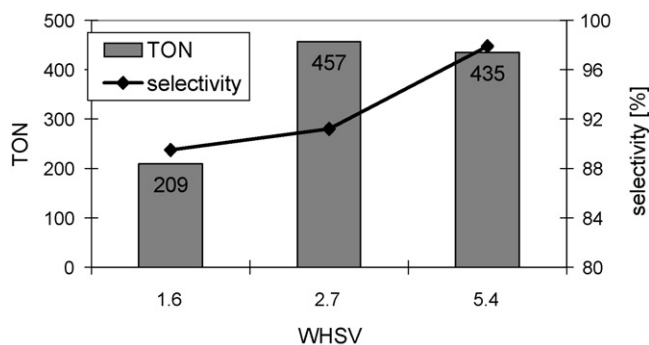


Fig. 3. TONs and selectivities for cyclooctane activation with the catalyst  $\text{IrH}(\text{CO})(\text{PPh}_3)_3$  (11) supported on  $\text{SiO}_2$  (Davicat SI1102).

conversions from alkanes to alkenes and hydrogen at higher temperatures can be expected because of the endothermic nature of this reaction.

The curves in Fig. 4 show an activation maximum which depends on the nature of the organometallic compound. The decrease of the TON after the maximum indicates decomposition of the active species at higher temperatures. For catalyst  $[\text{Ir}(\text{cod})(\text{Np-Tol}_3)_2]\text{PF}_6/\text{SiO}_2$  (7), no activation maximum was observed. These results reinforced the assumption that phosphorus participates in the formation and stabilization of the active species.

#### 2.5. Activities of iridium complexes on different supports

For standard experiments, the silica Davicat® SI1102 was used, a product of W.R.Grace & Co., Reg. USPTO. It has a surface area of  $311 \text{ m}^2/\text{g}$ , a pore volume of  $1.12 \text{ cc/g}$  and a pore diameter of  $144 \text{ \AA}$ . Due to these properties, it belongs to a group of standard silicas suitable for a broad range of applications. Because of the hypothesis that the catalytic centers are at the surface respectively in the pores of the support, it is obvious to investigate the influence of different surface areas, pore diameters and pore volumes. Therefore,  $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6$  was heterogenized on 25 different silica gels which can be classified in granular (Table 1) and powder silicas (Table 2).

The influence of the corresponding silica on the activity of the catalyst is obvious. The TONs varied between 115 and 667 depending on the silica. Generally, the granular silicas showed higher activities. There is also the fact that the granular silicas are easier to manage for the heterogenisation and the dehydrogenation experiments than the powder silicas. The highest TONs were obtained for a catalyst which was supported on silica SI1254 (surface area:  $567 \text{ m}^2/\text{g}$ , pore volume:  $0.81 \text{ cc/g}$ , pore diameter:  $57 \text{ \AA}$ ). The TON

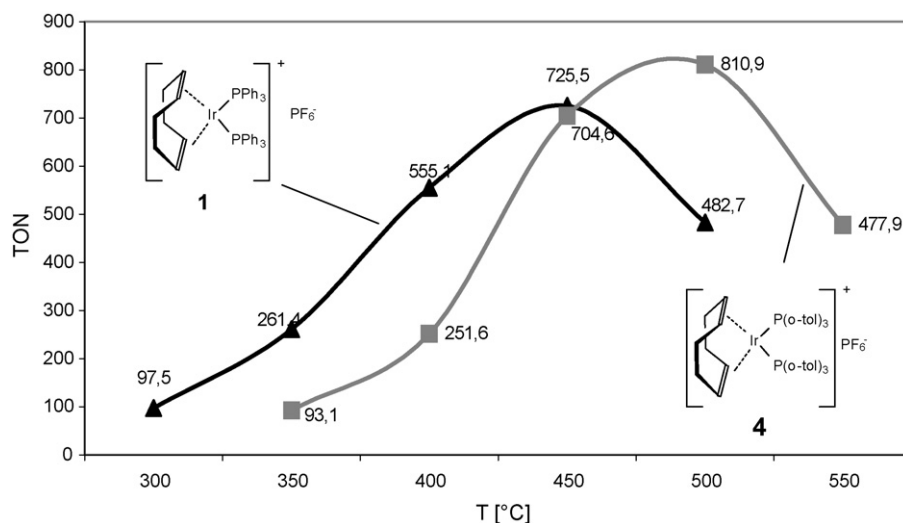


Fig. 4. Temperature dependence of the TONs in the dehydrogenation reactions of cyclooctane with catalysts 1 and 4.

**Table 1**  
TONs and selectivities of  $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6$  supported on different granular silicas

Support	Selectivity (%)	Conversion (%)	TON
SI1102	95.7	8.8	555.1
SI1101	98.6	2.7	173.5
SI1151	94.8	9.0	587.7
SI1251	85.7	4.5	283.8
SI1252	96.3	5.8	382.3
SI1253	80.7	7.8	463.7
SI1254	91.3	10.3	666.5
SI1600	95.2	7.3	460.2
SI1650	95.8	8.9	582.2
SI1700	96.3	9.3	572.1
Grade 57	96.3	8.7	552.1

was 667 (conversion: 10.3%) with a selectivity of 91.3%. Further products were the CH-activation products octahydropentalene, 2,4-octadiene and the isomerisation products methylcycloheptane and ethylcyclohexane. A special relationship between the catalyst activity and the properties of the applied silicas (surface area, pore diameter, pore volume) was not observed. Nevertheless, it is obvious that the silica properties influence the activity and the selectivity of the corresponding catalyst.

Besides silicas,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2/\text{Al}_2\text{O}_3$  supports were used for the heterogenisation of  $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6$ . The catalysts supported on  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2/\text{Al}_2\text{O}_3$  converted cyclooctane in a catalytic reaction. The activities were lower than those for catalysts supported

on  $\text{SiO}_2$ : TON = 318, 90, 281, 76 and 133. Remarkably, the activities of catalysts depend on the surface area and the pore diameter of the support. The catalyst supported on silica with the highest pore diameter and a lower surface area revealed the highest TON (318).

The catalysts with  $\text{Al}_2\text{O}_3$  as support showed the classic dehydrogenation reaction of cyclooctane to give cyclooctene. In contrast, the catalysts supported on  $\text{SiO}_2/\text{Al}_2\text{O}_3$  favoured the CH-activation reaction and produced octahydropentalene and isomerisation products (Fig. 5).

The catalysts supported on  $\text{TiO}_2$  and  $\text{ZrO}_2$  showed activities between 7 and 935 turnovers (Table 3). The activities depend on the titanium and zirconium content: The heterogeneous catalyst using the support with the lowest content of Ti (3.1%) resp. Zr (1.1%) had the highest TONs of 853 and 935. Nevertheless, a small Ti or Zr content has a positive effect on the activities. In comparison with the  $\text{TiO}_2$  and  $\text{ZrO}_2$  containing supports, the best catalyst on silica achieved a TON of 667 (1/SI1254).

The results showed that by choosing a suitable support material, the activity and the selectivity can be controlled. Generally, silica gels were the best commercial support materials for heterogeneous dehydrogenation catalysts. The silicas were only surpassed by MCM-41. MCM-41 was synthesized by hydrothermal procedures. Its structure consists of amorphous inorganic silica walls around surfactant molecules [35–37]. The catalyst  $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6$  sup-

**Table 2**  
TONs and selectivities of  $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6$  supported on different powder silicas

Support	Selectivity (%)	Conversion (%)	TON
SI1301	98.0	4.99	325
SI1302	93.6	4.58	296
SI1351	98.3	1.82	115
SI1401	94.2	2.40	150
SI1402	93.0	3.95	222
SI1403	84.1	7.08	249
SI1404	97.4	6.16	397
SI1405	96.9	7.58	477
SI1410	97.9	2.04	121
SI1415	96.0	7.73	500
SI1444	92.7	3.19	198
SI1451	91.0	6.81	454
SI1452	98.0	4.26	252
SI1454	96.5	4.42	265

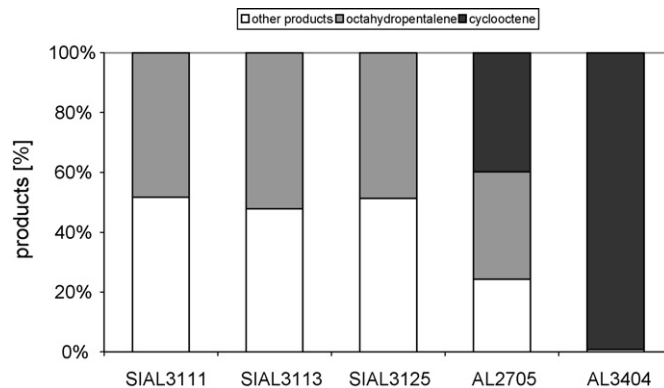


Fig. 5. Product distribution from the activation of cyclooctane induced from the catalyst  $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6$  supported on aluminum containing materials.

**Table 3**  
TONs of  $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6$  supported on  $\text{TiO}_2$  and  $\text{ZrO}_2$  containing materials

Support	SIT14850	SIT14552	SIT14551	SIT14550	SIZR4500	SIZR4700
Ti-/Zr- content (%)	7.0	5.2	3.1	3.1	3.7	1.1
Conversion (%)	0.11	3.73	9.55	12.94	2.70	12.90
TON	7	237	632	853	173	935

**Table 4**  
TON and selectivity of the catalyst  $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6/\text{MCM-41}$

Catalyst	$[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6$
Support	MCM-41
Selectivity (main product) (%)	92.0
Average TOF (/h)	202
Conversion (%)	16.06
TON	1009

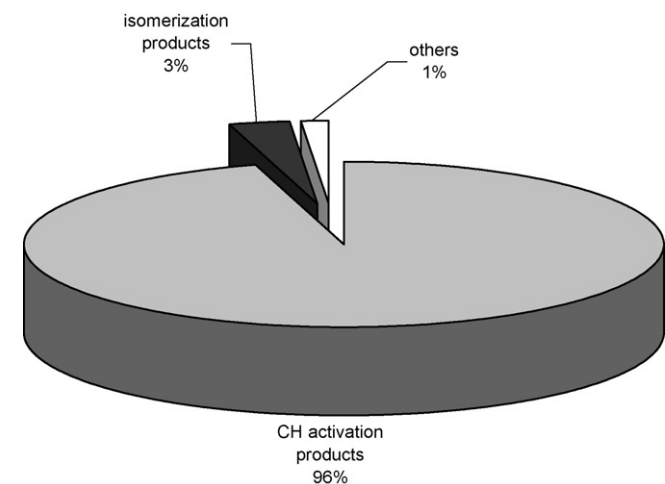
ported on MCM-41 showed an excellent activity of more than 1000 catalytic cycles in 5 h. This is equivalent to a conversion of 16.1%. The average TOF per hour was 202 (Table 4).

Besides this high activity, an excellent selectivity of 96% for the dehydrogenation products was achieved (Fig. 6). The CH-activation products were cyclooctene (92%) and octahydropentalene (4%).

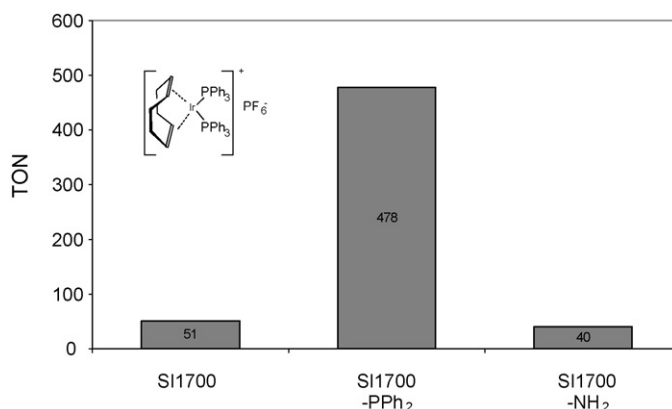
Another method to influence the activity and selectivity of a heterogeneous catalyst is to functionalize the support material with amine or phosphine groups. The functional groups can undergo reactions with the metal centers of the organometallic compounds forming a new type of complex. The catalyst  $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6$ , fixed on the amine functionalized support material, showed no activity change. The same catalyst on PPh<sub>2</sub> functionalized silica gave a 1000% higher activity (TON = 478) (Fig. 7).

## 2.6. Influence of additives on heterogeneous dehydrogenation reactions

Regarding the structure–efficiency relationships, it became evident that the nature of the heteroatom containing ligands has a relevant impact on the activities of the corresponding catalysts. Therefore, it is obvious that an external additive (ratio of metal:additive = 1:4), like an amine or a phosphine also influences the heterogeneous catalysts. The addition of amines and KO<sup>t</sup>Bu did not increase the activity. The TONs were between 17 and 61. In comparison to these results, a catalyst without any additives revealed a TON of 38 (Table 5). The selectivities of these catalysts were lower than in case of no external additives.



**Fig. 6.** Product distribution from the activation of cyclooctane with  $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6$  supported on MCM-41.



**Fig. 7.** TONs of  $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6$  supported on functionalized support materials.

**Table 5**  
TONs and selectivities of the catalyst  $([\text{Ir}(\text{cod})\text{Cl}]_2/\text{SiO}_2)$  (12) with different external additives

External additive	Molar ratio M:P	Selectivity (%)	Conversion (%)	TON
–	–	93.8	0.6	38
NPh <sub>3</sub>	1:2	76.6	0.5	31
N( <i>p</i> -Tol) <sub>3</sub>	1:4	83.8	0.3	17
NH <sub>2</sub> Ph	1:4	82.8	0.6	36
NH( <i>i</i> -Prop) <sub>2</sub>	1:4	78.3	0.7	41
KO <sup>t</sup> Bu	1:4	92.3	0.9	61

The addition of phosphines to the heterogeneous catalyst  $[\text{Ir}(\text{cod})\text{Cl}]_2$ , supported on  $\text{SiO}_2$  (SI1102), achieved a general increase of the activities. The catalysts showed TONs between 111 and 834. In case of triphenylphosphine (metal:additive = 1:4), the activity was more than 2000% higher than for catalyst 12 without an external additive (Table 6). The best ratio of metal to additive was 1:4. Almost all phosphine additives lead to higher selectivities than 12 (without additive). These catalysts produced cyclooctene with selectivities of 94.0–98.1% (Table 6).

The heterogeneous phosphine ligand containing catalysts 1–5 obviously produced cyclooctene with higher activities than  $[\text{Ir}(\text{cod})\text{Cl}]_2/\text{SiO}_2$  (12). Despite the generally high TONs of the phosphine containing catalysts (TON = 252–582), the addition of triphenylphosphine increased the activity up to a TON of 910

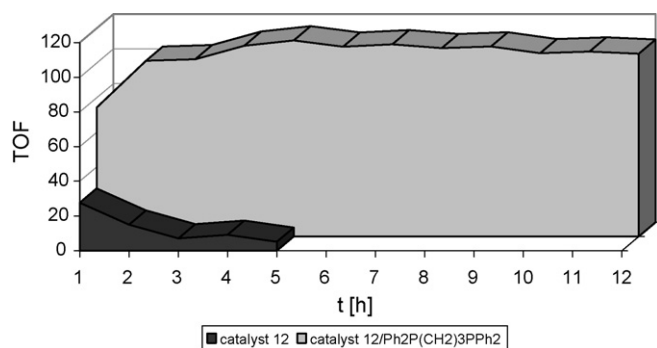
**Table 6**  
TONs and selectivities of the catalysts  $([\text{Ir}(\text{cod})\text{Cl}]_2/\text{SiO}_2)$  (12) with different external additives

External additive	Molar ratio M:P	Selectivity (%)	Conversion (%)	TON
–	–	93.8	0.6	38
PPh <sub>3</sub>	1:2	97.2	6.5	409
PPh <sub>3</sub>	1:4	96.2	11.6	834
P( <i>p</i> -Tol) <sub>3</sub>	1:4	96.3	11.2	704
P( <i>o</i> -Tol) <sub>3</sub>	1:4	97.5	7.8	491
P( <i>m</i> -Tol) <sub>3</sub>	1:4	94.6	12.1	774
PCy <sub>3</sub>	1:4	96.2	8.6	548
P( <i>n</i> -Bu) <sub>3</sub>	1:4	98.0	3.9	245
Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>3</sub> PPh <sub>2</sub>	1:4	98.1	8.0	500
P(C <sub>6</sub> H <sub>4</sub> Cl) <sub>3</sub>	1:4	94.0	7.2	487
P(Benz) <sub>3</sub>	1:4	86.6	1.7	111

**Table 7**

TONs and selectivities of the catalyst  $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6/\text{SiO}_2$  (**1**) and combinations with various phosphines and additives

External additive	Molar ratio M:P	Selectivity (%)	Conversion (%)	TON
–	–	96.7	8.7	582
$\text{PPh}_3$	1:4	93.3	13.8	910
$\text{P}(p\text{-Tol})_3$	1:4	95.4	7.7	505



**Fig. 8.** Increase of the activity and the longtime stability of catalyst **12** after the addition of the external phosphine ( $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ ).

(Table 7). This TON is similar to a conversion of almost 14% with a selectivity of 93.3% for the production of cyclooctene.

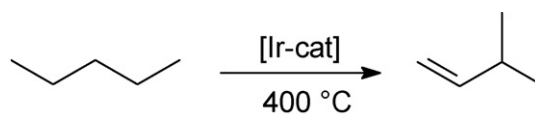
Besides the increase of the activity, special additives lead to an enormous increase of the long time stability of the corresponding catalyst (Fig. 8). The TOFs were found to be rather constant for a reaction time of 12 h. Different from this result, the TOFs of catalyst **12** (without additive) decreased from 28 to 5 within 5 h.

**Table 8**

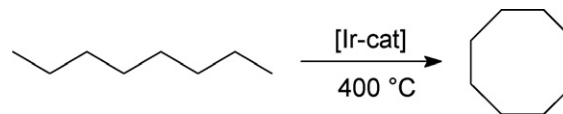
TONs and selectivities of catalysts **3**, **8** and **9** for the dehydrogenation of *n*-pentane and *n*-octane

Catalyst <sup>a</sup>	Alkane	Main product	Selectivity (%)	TON
	<i>n</i> -Pentane	1-Isopentene	52.3	110
	<i>n</i> -Octane	Cyclooctane	89.7	342
	<i>n</i> -Pentane	1-Isopentene	36.0	11
	<i>n</i> -Octane	Cyclooctane	71.9	75
	<i>n</i> -Pentane	1-Isopentene	52.2	40
	<i>n</i> -Octane	Cyclooctane	72.6	43

<sup>a</sup> The coordination compound was heterogenized on silica gel SI1102.



**Scheme 3.** Dehydrogenation of *n*-pentane with the iridium catalysts **3**, **8** and **9**.



**Scheme 4.** Dehydrogenation of *n*-octane with the iridium catalysts **3**, **8** and **9**.

### 2.7. Dehydrogenation reactions of linear alkanes with heterogeneous iridium catalysts

Besides cyclooctane, also the linear alkanes *n*-pentane and *n*-octane which are more difficult to activate were used for CH-activation reactions. The investigated catalysts **3**, **8** and **9** were able to activate these linear alkanes (Table 8). The catalyst  $[\text{Ir}(\text{cod})(\text{P}(p\text{-Tol})_3)_2]\text{PF}_6$ , supported on SI1102 (**3**), exhibited the highest TONs for dehydrogenation reactions of linear alkanes: the TON for *n*-pentane was 110, *n*-octane was activated with a TON of 342.

The dehydrogenation of *n*-pentane was accompanied by an isomerisation process to produce 1-isopentene (Scheme 3).

The activation of *n*-octane resulted in cyclooctane which was produced in a combination of a dehydrogenation and a cyclization reaction (Scheme 4).

### 2.8. Comparison of cobalt, rhodium and iridium carbonyl cluster complexes

Dehydrogenation experiments with the heterogenized, tetrameric carbonyl clusters  $\text{M}_4(\text{CO})_{12}$  as catalysts ( $\text{M}=\text{Co}$  (**13**), Rh

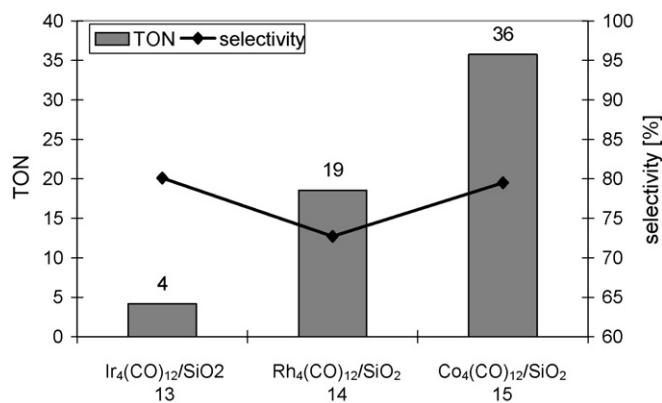


Fig. 9. Comparison of the dehydrogenation potential of the tetrameric carbonyl cluster complexes  $\text{M}_4(\text{CO})_{12}$  ( $\text{M}=\text{Co}, \text{Rh}, \text{Ir}$ ).

(14), Ir (15) resulted in a catalytic conversion of cyclooctane. The  $\text{M}_4(\text{CO})_{12}/\text{SiO}_2$  catalysts achieved different activities depending on the metal. The following activity range was found: Co (TON = 4) < Rh (TON = 19) < Ir (TON = 36) (Fig. 9).

The reason for the different activities of catalysts 13–15 is probably the increase of the noble character of the metal center from cobalt to iridium. The lower activity of the rhodium containing catalyst in contrast to the iridium containing catalyst can be explained by the different binding properties: The ability of rhodium to form stable complexes with (-ligands (low excitation energy of rhodium favours the (-back bonding [38]) can make the release of the generated olefin more difficult. The catalysts are poisoned by their own products.

### 3. Summary and conclusion

Novel heterogeneous catalysts were synthesized by using different support materials like  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , MCM-41 and they were tested for thermal CH-activation reactions in a fixed bed reactor. The activities of the iridium containing catalysts showed a strong dependence of the ligand system. Excellent results were obtained with  $[\text{Ir}(\text{cod})(\text{PR}_3)_2]\text{PF}_6/\text{SiO}_2$  catalysts ( $\text{R}=\text{Ph}, \text{Cy}, p\text{-Tol}, m\text{-Tol}, o\text{-Tol}$ ) (1–5). Their phosphine ligands are supposed to be an essential component of new active species formed at higher temperatures. For a more detailed investigation of this context, a certain amount of phosphine was added during the synthesis of the catalyst. Respectively, a functionalized support material was used. In these cases, an increase of the activities was achieved. The addition of external triphenylphosphine provided a TON of 834 (12/ $\text{PPh}_3$ ) which is an increase of more than 2000%. In contrast to the phosphines, the addition of amines did not give a positive effect. The variation of the reaction conditions showed a strong dependence of the temperature, with an activity maximum depending on the organometallic compound. Furthermore, the WHSV could be optimized, an important feature for an industrial application. The upper limit is the reaction rate. The alkane needs a certain residence time at the catalyst for a complete reaction. The synthesized catalysts worked with relatively high WHSVs (2.7–5.4) and showed excellent conversion rates and selectivities. The application of the heterogeneous catalysts on different supports in CH-activation experiments proved the enormous impact of the support material on the activities and selectivities. The dehydrogenation results provided an activity and selectivity control by choosing a suitable support. Generally, silica gels were the best commercial support materials for heterogeneous dehydrogenation catalysts. The silicas were only surpassed by MCM-41. The cata-

lyst ( $[\text{Ir}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6/\text{MCM-41}$ ) showed an excellent activity of more than 1000 catalytic cycles in 5 h, corresponding to a conversion rate of 16.1%. Besides this high activity, an excellent selectivity of 96% for dehydrogenation products was achieved. The answer for the question of the nature of the actual catalyst at higher temperatures is still open. The organometallic complex in combination with the support material and the additive could form such a catalytic species consisting of a multinuclear heteroatomic cage or nanocluster on the surface of the support material. We exclude the formation of finely dispersed iridium as a catalyst because of the strong influence of the support and additives and because it is known that such catalysts predominantly cleave CC bonds and not CH bonds [39]. On the other side it is known that catalytically active metals like platinum readily undergo reactions with heteroatom containing substrates like sulfides [40].

## 4. Experimental

### 4.1. General considerations

All manipulations were carried out using standard Schlenk techniques under argon, which was purified with a BTS catalyst and molecular sieves (4 Å). The dehydrogenation experiments were performed in a fixed bed reactor which was designed for the special conditions of heterogeneous CH-activation reactions. A gas chromatograph Agilent 6890 was used to monitor the dehydrogenation reactions. Argon was applied as carrier gas, a 30 m HP-5 column (5% phenyl methyl siloxane) 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 identification of the dehydrogenation products and the reaction control were carried out by a FOCUS DSQ (TM) instrument. Argon was applied as carrier gas, a 30 m TR-5MS (5% phenyl(equiv) polysilphenylene-siloxane) 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).

### 4.2. Materials

Tetrahydrofuran, *n*-pentane and toluene were distilled from Na/K alloy. Methylene chloride was distilled from  $\text{P}_2\text{O}_5$ . All solvents were stored under argon. Cyclooctane (COA) was degassed and stored under argon. The support materials were purchased from Davison Catalysts. The complexes  $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ ,  $\text{Ir}_4(\text{CO})_{12}$ ,  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{Co}_4(\text{CO})_{12}$  were purchased from Strem Chemicals, Inc.  $[\text{Ir}(\text{cod})\text{Cl}]_2$  was synthesized in analogy to known procedures [41].

### 4.3. Synthesis of the functionalized support materials

A solution of 4 mmol functionalisation reagent (2-(diphenylphosphine)ethyl-triethoxysilane, 3-aminopropyl-trimethoxysilane) in 15 ml of *n*-pentane and 15 ml  $\text{Et}_2\text{O}$  were added to 14 g of silica. The suspension was heated to reflux for 24 h. After filtration, the functionalized silica was washed with *n*-pentane and dried in vacuo.

### 4.4. Preparation of heterogeneous catalysts

The heterogeneous catalysts were synthesized by the incipient wetness method. For this purpose, the amount of solvent ( $\text{CH}_2\text{Cl}_2$ , THF) that can be absorbed by the support material has to be determined. To 1 g of silica was added dropwise the desired solvent until the liquid was visible around the particles. The amount of solvent could be calculated by the weight difference.

For heterogenisation, the coordination compound was dissolved in the calculated amount of solvent required to fill all pores of the support. The solution was added to 3 g of the corresponding support. After evaporation of the solvent in vacuo, the heterogeneous catalyst could be used for dehydrogenation experiments in a fixed bed reactor. The content of metal on the support was 0.35 wt.%.

#### 4.5. Addition of external additives to the heterogeneous catalysts

A solution of the desired additive (molar ratio M:additive = 1:2, 1:4) dissolved in CH<sub>2</sub>Cl<sub>2</sub> was added to the heterogeneous catalyst and the solvent was evaporated in vacuo.

#### 4.6. Heterogeneous dehydrogenation experiments

The heterogeneous catalyst was fixed in the reactor tube between glass wool. After connecting the reactor tube with the pipe system of the fixed bed reactor, the tube was heated up to 350–550 °C. The standard reaction temperature was 400 °C with a reaction time of 5 h. The temperature control was inside the reaction tube. The desired alkane (cyclooctane, *n*-octane, isopentane) was pumped with a constant flow (WHSV=2.7) over the catalyst bed. The products were collected in a cooled Schlenk tube and analyzed hourly by gas chromatography. The product identification was carried out by GC/MS or by using reference compounds.

#### Acknowledgement

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

#### References

- [1] R.H. Crabtree, *J. Chem. Soc. Dalton Trans.* (2001) 2437.
- [2] C.M. Jensen, *Chem. Commun.* (1999) 2443.
- [3] R.H. Crabtree, J.M. Mihelcic, J.-M. Quirk, *J. Am. Chem. Soc.* 101 (1979) 7738.
- [4] J.H. Hoyano, W.A.G. Graham, *J. Am. Chem. Soc.* 104 (1982) 3723.
- [5] R.G. Bergman, A.H. Janowicz, *J. Am. Chem. Soc.* 104 (1982) 352.
- [6] D. Baudry, M. Ephritikhine, H. Felkin, R. Holmes-Smith, *J. Am. Chem. Soc.* (1983) 788.
- [7] M.J. Burk, R.H. Crabtree, C.P. Parnell, R.J. Uriarte, *Organometallics* 3 (1984) 816.
- [8] H. Felkin, T. Fillebeen-Khan, Y. Gault, R. Holmes-Smith, J. Zakrzewski, *Tetrahedron Lett.* 25 (1984) 1999.
- [9] M.J. Burk, R.H. Crabtree, D.V. McGrath, *J. Chem. Soc. Chem. Commun.* (1985) 1829.
- [10] M. Gupta, C. Hagen, R.J. Flesher, W.C. Kaska, C.M. Jensen, *Chem. Commun.* (1996) 2083.
- [11] R.H. Crabtree, C.P. Parnell, *Organometallics* 4 (1985) 519.
- [12] M.J. Burk, R.H. Crabtree, *J. Am. Chem. Soc.* 109 (1987) 8025.
- [13] J.A. Maguire, W.T. Boese, A.S. Goldman, *J. Am. Chem. Soc.* 111 (1989) 7088.
- [14] J.A. Maguire, A.S. Goldman, *J. Am. Chem. Soc.* 113 (1991) 6706.
- [15] J.A. Maguire, A. Petrillo, A.S. Goldman, *J. Am. Chem. Soc.* 114 (1992) 9492.
- [16] J. Belli, C.M. Jensen, *Organometallics* 15 (1996) 1532.
- [17] P. Braunstein, Y. Chauvin, J. Nahring, A. DeCian, J. Fischer, A. Tiripicchio, F. Ugazolli, *Organometallics* 15 (1996) 5551.
- [18] J.A. Miller, L.K. Knox, *J. Chem. Soc. Chem. Commun.* (1994) 1449.
- [19] I. Göttker-Schnetmann, P. White, M. Brookhart, *J. Am. Chem. Soc.* 126 (2004) 1804.
- [20] R.H. Crabtree, G.E. Morris, *J. Organomet. Chem.* 135 (1977) 395.
- [21] R.H. Crabtree, H. Felkin, G.E. Morris, *J. Organomet. Chem.* 141 (1977) 205.
- [22] D. Hesk, P.R. Das, B. Evans, *J. Labelled Compd. Radiopharm.* 36 (1995) 497.
- [23] S. Taubmann, PhD Thesis, Universität Bayreuth 2007.
- [24] L. Carlton, J.J. Molapisi, *J. Organomet. Chem.* 609 (2000) 60.
- [25] J. Blümel, *J. Am. Chem. Soc.* 117 (1995) 2112.
- [26] K.D. Behringer, J. Blümel, *J. Liq. Chromatogr.* 19 (1996) 2753.
- [27] N.J. Meehan, A.J. Sandee, J.N.H. Reek, P.C.J. Kamer, P.W.N.M.v. Leeuwen, M. Poliakoff, *J. Chem. Soc. Chem. Commun.* (2000) 1497.
- [28] H. Yang, H. Gao, R.J. Angelici, *Organometallics* 19 (2000) 622.
- [29] B.K. Das, J.H. Clark, *J. Chem. Soc., Chem. Commun.* (2000) 605.
- [30] Y. Wang, T.J. Su, R. Green, Y. Tang, D. Styrkas, T.N. Danks, R. Bolton, J.R. Lu, *J. Chem. Soc. Chem. Commun.* (2000) 587.
- [31] A. Corma, M. Iglesias, F. Mohino, *J. Organomet. Chem.* 544 (1997) 147.
- [32] C. Merckle, J. Blümel, *Adv. Synth. Catal.* 345 (2003) 584.
- [33] C. Merckle, S. Haubrich, J. Blümel, *J. Organomet. Chem.* (2001) 44.
- [34] I. Böhmer, *Homogene und heterogene Katalysatoren für CH-Aktivierungsreaktionen von gesättigten Kohlenwasserstoffverbindungen*, vol. 1, *ibidem*, Stuttgart, 2003.
- [35] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, *J. Am. Chem. Soc.* 114 (1992) 10834.
- [36] C.-Y. Chen, H.-X. Li, M.E. Davis, *Microporous Mater.* 2 (1993) 17.
- [37] Z. Luan, C.-F. Cheng, W. Zhou, J. Klinowski, *J. Phys. Chem.* 99 (1995) 1018.
- [38] A.F. Holleman, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, 101 ed., de Gruyter, Berlin, 1995.
- [39] A. Majesté, S. Balcon, M. Guérine, C. Kappenstein, Z. Paál, *J. Catal.* 187 (1999) 486.
- [40] Z. Paál, M. Muhler, K. Matisek, *J. Catal.* 175 (1998) 245.
- [41] J.L. Herde, J.C. Lambert, C.V. Senoff, *Inorg. Syn.* 15 (1974) 18.