Homogeneous and heterogeneous dehydrogenation reactions of cyclooctane with palladium(II) complexes as catalysts

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ABSTRACT

A series of new palladium(II) complexes with heteroatomic chelating ligands (carboxylates and alcoholates) was synthesized. The catalytic activities of the palladium complexes were successfully tested for catalytic CH-activation reactions of cyclooctane. They gave TONs of 2.6–26.5 (300 °C, 16 h) in homogeneous solution and 4.6–21.4 (400 °C, 5 h) in heterogeneous reactions.

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1. Introduction

The activation of chemical bonds especially of C—H bonds represents an important research goal. Saturated hydrocarbons are abundant and still comparatively inexpensive chemical feedstocks [1] but the selective synthesis of functional products directly from alkanes under mild conditions remains a prominent challenge in research. Current industrial organic processes largely depend on alkenes which are produced by thermal decomposition of alkanes. This cracking process, however, needs temperatures up to 1000 °C [2] and it requires an expensive separation and purification process because a complex mixture of products is produced. Consequently, a new selective method for alkene production under mild conditions is desirable. The CH-activation of alkanes via oxidative addition at the metal center of transition metal complexes is one of the most promising approaches to the target. So far, dehydrogenation reactions of alkanes have been carried out mainly with the metals rhodium and iridium [3–9], and heteroatom functionalizations mostly with platinum [10–13]. The activation of CH bonds with palladium complexes in homogeneous solution is known but reports are rare [14,15]. The activation reaction is mostly involved with a functionalization of the alkane. A direct dehydrogenation of the alkane to give an alkene has not

been described. Another big disadvantage is the fact that hydrogen acceptors (e.g. *tert*-butylethylen) are needed [16–21]. This makes such a reaction uneconomic for an industrial process.

In this contribution four-coordinated palladium(II) complexes have been synthesized and characterized and were tested for the catalytic CH-activation of cyclooctane in homogeneous and heterogeneous systems without any hydrogen acceptors.

## 2. Results and discussion

2.1. Complex synthesis

The carboxylate palladium(II)complexes can be synthesized by a direct conversion of Pd(OAc)$_2$ with 2 equiv. of the corresponding carboxylic acid. The complexes were formed by ligand exchange with a transfer of the carboxyl proton to the acetate (Scheme 1). The formed acetic acid can be removed by evaporation of the solvent and washing of the residue with water. Complexes **1a**–**e** were obtained with yields of 84–95%.

A similar complex type as the carboxylate palladium(II)complexes are the alcoholate palladium(II)complexes. The complexes **2a** and **2b** cannot be synthesized by direct conversion of PdCl$_2$ and the corresponding alcohol. The ligand precursors have to be transformed into the corresponding sodium alcoholates. The typical procedure for the synthesis was the following: the ligand precursor reacts with NaH to give the sodium alcoholate and hydrogen. The reaction of 1 equiv. of these alcoholate ligand precursors with 0.5 equiv. of PdCl$_2$ yields **2a** and **2b** (Scheme 2).

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E-mail address: helmut.alt@uni-bayreuth.de (H.G. Alt).
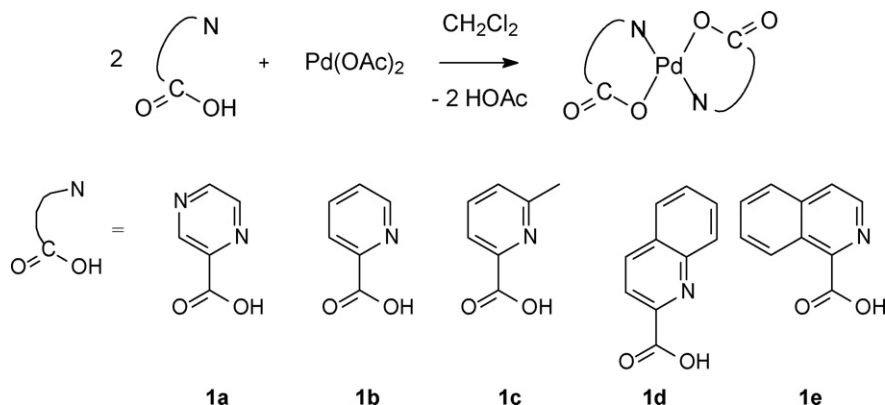
Scheme 1. Synthesis of carboxylate palladium(II) complexes.
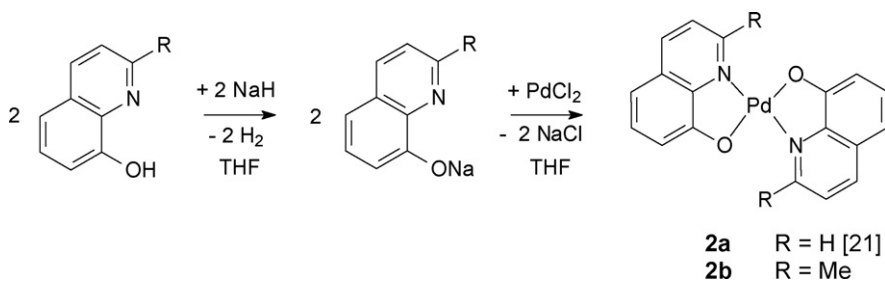
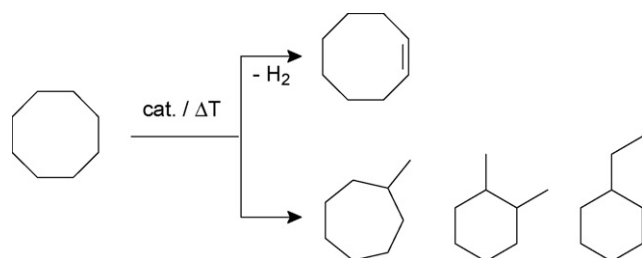Scheme 2. Synthesis of alcoholate palladium(II) complexes.

2.2. Homogeneous dehydrogenation of cyclooctane

The palladium complexes were tested as catalysts for the dehydrogenation of cyclooctane at 300 °C. Cyclooctane reacts to give cyclooctene as main product, along with small amounts of the isomerisation products 1,2-dimethylcyclohexane, ethylcyclohexane and methylcycloheptane (Scheme 3).

A temperature/TON diagram indicates that most catalysts do no longer have their original compositions at reaction temperatures above 350 °C. Nevertheless the catalysts were active up to 400 °C (Scheme 4). The catalysts produced cyclooctene as the main product.

The CH-activation is an endothermic reaction. Higher temperatures lead to higher activities providing the same active species. The increased TONs at 375 resp. 400 °C show that the active species are highly temperature resistant as well as it is safe to assume that the coordination compounds 1d and 2a do no longer exist in their original composition at these temperatures. Instead, a new catalytic species must be formed. This new active species could not be identified so far.

There is a structure–efficiency relationship although the catalysts changed their composition (Scheme 5). The highest

turnover numbers of 1b and 1d were 18 and 16. A detailed structure–efficiency relationship could not be recognized, the activity differences of catalysts 1b–d and 2a–b show that the ligands have a significant influence in building and stabilizing the new active species. All catalysts have in common a high selectivity of 88–95% (Scheme 5).

A positive influence of phosphines on the activity of iridium catalysts is known [22]. On this basis, different Lewis bases of group 15 elements were investigated as additives for 1d for the CH-activation of cyclooctane (Table 1).

A positive effect of phosphine additives could not be found for the investigated palladium catalysts. On the contrary, the phosphines decreased the activity of 1d. In comparison, the addition of certain amine additives (3e and 3g) had a positive effect on the activity. Especially catalyst 3e showed a 60% higher TON than 1d (without any additive). The role of these additives is unclear. Obvi-

Scheme 3. Activation of cyclooctane.
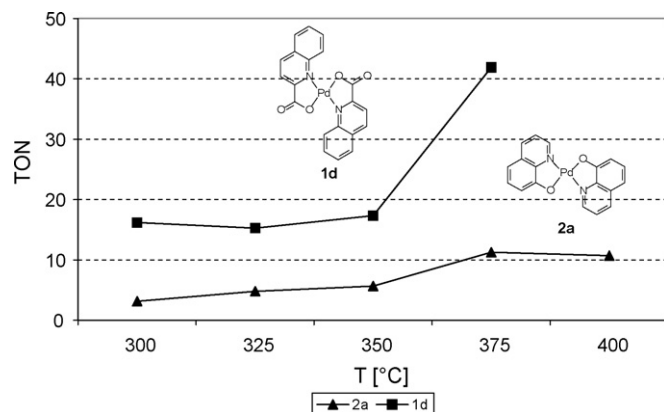
Scheme 4. Activities of 1d and 2a at different temperatures.
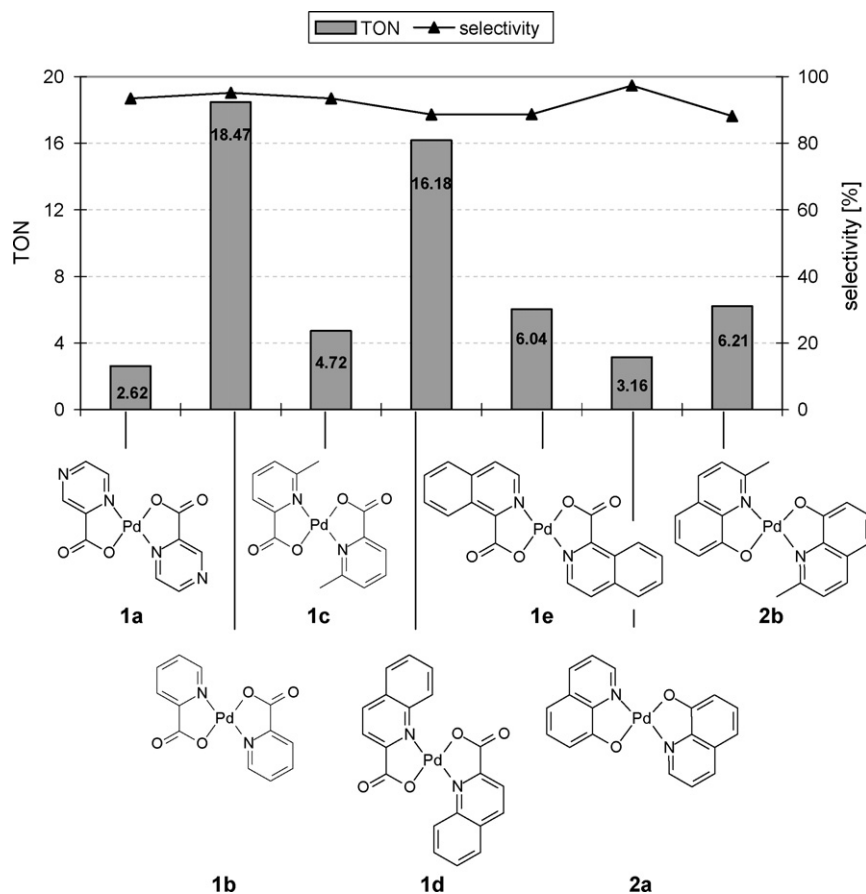
Scheme 5. Activity and selectivity of **1b–d** and **2a–b**.

ously they participate in the formation of a new active species but they can also block the active site of such a catalyst.

2.3. Heterogeneous dehydrogenation of cyclooctane

For industrial applications of catalytic CH-activation, the heterogenization of catalysts is necessary.

The catalysts were prepared by the "incipient wetness" method. Catalysts **4a–c** were prepared by supporting the imaged palladium complexes on silicagel (Davicat© SI1102). The CH-activation experiments were performed at 400 °C for 5 h in a fixed-bed reactor.
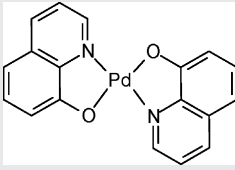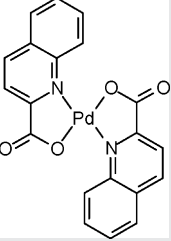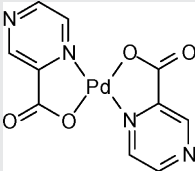
The catalysts with carboxylate ligands (**4b** and **4c**) gave slightly higher TONs than the alcoholate containing catalyst **4a** (Table 2).

The lower alkane flow (WHSV = 1.2) induced a little smaller TON of 9.2 (**4b**), as there is less cyclooctane provided in the same time. The contact time of the alkane and the active species is already sufficient at a WHSV of 2.6.

Table 1
Activity and selectivity of **1d** with different additives

Additives	No.	TON	Selectivity (%)
–	**1d**	16.2	88.6
P(n-Bu)$_3$	**3a**	4.8	73.0
PPh$_3$	**3b**	6.1	86.2
N(n-Bu)$_3$	**3c**	9.2	90.0
NPh$_3$	**3d**	16.3	97.1
NTol$_3$	**3e**	26.5	96.5
NHPh$_2$	**3f**	11.2	94.5
NH$_2$Ph	**3g**	18.9	94.3
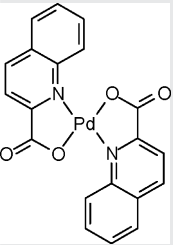
Table 2
Activities and selectivities of catalysts **4a–d**

Complex	No.	WHSV	Average TOF	TON	Selectivity (%)
	4a	2.6	1.95	9.9	75
	4b	2.6	2.10	11.9	77
		1.2	1.75	9.2	58
	4c	2.6	2.26	12.0	67
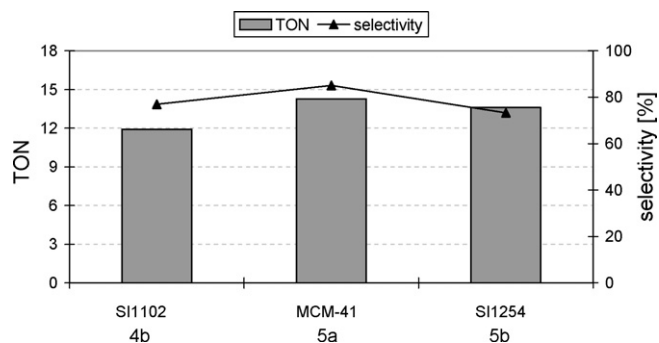
Scheme 6. Activity and selectivity of **4b**, **5a** and **5b**.

Table 3
Activities and selectivities of **4b**, **6a** and **6b**

Complex	Additive	No.	Average TOF	TON	Selectivity (%)
	–	**4b**	2.10	11.93	77
	PPh$_3$	**6a**	3.99	21.39	71
	NTol$_3$	**6b**	1.28	4.56	29

Besides the palladium complexes also the support material had an influence on the activity of the complexes. Complex **1d** was supported on different materials: Davicat© SI1102, MCM-41 and Davicat© SI1254. MCM-41 were synthesized by a mesophase-template-mechanism according to Kresge et al. [23–26]. The support materials MCM-41 and SI1254 with a larger surface and a smaller pore diameter gave a slightly higher TON (Scheme 6).

The addition of Lewis bases had a converse effect on the activity than in homogeneous activation experiments: the phosphine increased the activity by almost 100%, the amine decreased the activity by 100% (Table 3).

3. Summary and conclusion

The novel palladium(II) complexes **1a**–**e** and **2b** which contain N,O-chelating ligands were synthesized. These complexes are air and moisture resistant and allow an easier handling in catalysis.

In the literature there exist no bench marks for palladium complexes in homogeneous and especially not in heterogeneous CH-activation reactions without any hydrogen acceptors. A comparison with known iridium systems show that palladium containing catalysts range behind the iridium systems. All tested catalysts catalyzed the CH-activation of cyclooctane in homogeneous and heterogeneous systems. They had TONs of 2.6–26.5 (300 °C, 16 h) in homogeneous catalysis and 4.6–21.4 (400 °C, 5 h) in heterogeneous catalysis. The TONs were clearly influenced by the ligand structure and the nature of the Lewis basic additives. The addition of certain additives like NTol$_3$ increased the activities. In heterogeneous catalysis, the CH-activation was influenced by the support material. In comparisons, catalysts with supports that had a larger surface and a smaller pore diameter were advantageous for the dehydrogenation of cyclooctane.

4. Experimental

4.1. General considerations

Air- and moisture-sensitive reactions were carried out under an atmosphere of purified argon using conventional Schlenk techniques. Elemental analysis was determined with 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 by GC (Agilent 6890) and GC/MS (FOCUS DSQ^{TM} instrument (Thermo Scientific)). 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 registered 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).

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 attached mineral oil. Cyclooctane (COA) was degassed and stored under argon. The organic starting materials were purchased from Aldrich or Arcos and were used without any purification.

4.3. General procedure for the synthesis of carboxylate palladium(II) complexes (1)

2 mmol of the respective carboxylic acid was dissolved in 30 ml CH$_2$Cl$_2$. 1 mmol of Pd(OAc)$_2$ was added, and the solution was stirred for 20 h at room temperature. The CH$_2$Cl$_2$ was evaporated after the addition of deionized water. The precipitating solid was removed by filtration, washed with water and pentane. After drying in vacuo the complexes were obtained as yellow solids, nearly insoluble in organic solvents.

(**1a**). From 0.25 g (2 mmol) of pyrazine carbonic acid and 0.22 g (1 mmol) Pd(OAc)$_2$ was obtained 0.32 g (0.91 mmol, 91%) of **1a** as a light yellow powder. Anal. Calc. for C$_{10}$H$_6$N$_4$O$_4$Pd (**1a**): C: 34.06; H: 1.72; N: 15.89. Found: C: 35.18; H: 2.25; N: 15.17. MS data for **1a**: 352 (M$^{•+}$) (1), 308 (1), 264 (100), 185 (14) 158 (21) 80 (100).

(**1b**). From 0.35 g (2 mmol) of picolinic acid and 0.22 g (1 mmol) Pd(OAc)$_2$ was obtained 0.33 g (0.95 mmol, 95%) of **1b** as a yellow powder. MS data for **1b**: 272 (M$^{•+}$) (8), 184 (62), 106 (59).

(**1c**). From 0.29 g (2 mmol) of 6-methyl picolinic acid and 0.22 g (1 mmol) Pd(OAc)$_2$ was obtained 0.33 g (0.87 mmol, 87%) of **1c** as a yellow powder. Anal. Calc. for C$_{14}$H$_{12}$N$_2$O$_4$Pd (**1c**): C: 44.41; H: 3.19; N: 7.40. Found: C: 45.05; H: 3.39; N: 7.34. MS data for **1c**: 378 (M$^{•+}$) (10), 290 (48), 198 (8), 184 (100) 92 (60).

(**1d**). From 0.35 g (2 mmol) of quinoline 2-carbonic acid and 0.22 g (1 mmol) Pd(OAc)$_2$ was obtained 0.40 g (0.89 mmol, 89%) of **1d** as a yellow powder. MS data for **1d**: 450 (M$^{•+}$) (0.5), 362 (22), 129 (100).

(**1e**). From 0.35 g (2 mmol) of isoquinoline carbonic acid and 0.22 g (1 mmol) Pd(OAc)$_2$ was obtained 0.38 g (0.84 mmol, 84%) of **1e** as a yellow powder. Anal. Calc. for C$_{20}$H$_{12}$N$_2$O$_4$Pd (**1e**): C: 53.29; H: 2.68; N: 6.21. Found: C: 52.92; H: 3.00; N: 5.62. MS data for **1e**: 450 (M$^{•+}$) (0.5), 362 (18), 129 (48).

4.4. Synthesis of the alcoholate palladium(II) complex **2b**

In 30 ml of THF an amount of 0.05 g (2 mmol) NaH was dissolved. 0.32 g (2 mmol) 2-methyl-8-hydroxyquinoline were added and the

Table 4
Properties of different support materials

	SI1102	SI1254	MCM-41 [27]
Surface (m^2/g)	311	567	765
Pore volume (cm^3/g)	1.12	0.81	–
Pore diameter (Å)	144	57	34

mixture was stirred for 2 h at room temperature. 0.18 g (1 mmol) $PdCl_2$ was then added and the mixture was stirred for 2 h. The solvent was evaporated in high vacuum, the residue was suspended in CH_2Cl_2. After filtration of the solution over Na_2SO_4, the solvent was evaporated. The residue was washed with 50 ml pentane and dried in vacuo. The complex was obtained as yellow powder with a yield of 85%.

MS data for **2b**: 422 ($M^{\bullet+}$) (46), 263 (26), 159 (100), 131 (93).

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. The solution was transferred into an 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 was analyzed by GC.

4.6. Preparation of the heterogeneous catalysts by "incipient wetness"

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

An amount of 17–19 mg of the palladium complex was dissolved in the calculated amount of CH_2Cl_2 and this solution was added slowly to 3 g support material. The solvent was evaporated in a vacuum. With this method the catalysts **4a**–**c**, **5a** and **5b** were prepared. Support materials with different properties were used (Table 4).

4.7. Heterogeneous dehydrogenation of cyclooctane

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

Acknowledgment

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