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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.

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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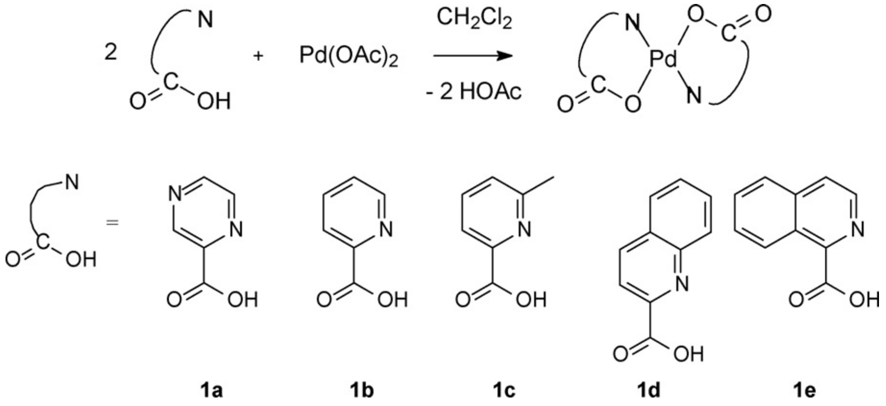
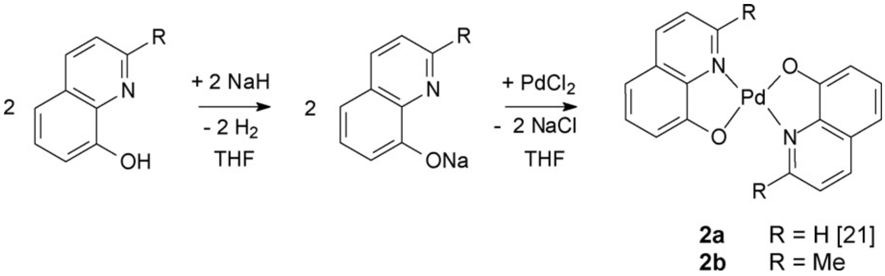


Scheme 1. Synthesis of carboxylate palladium(II) complexes.



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).

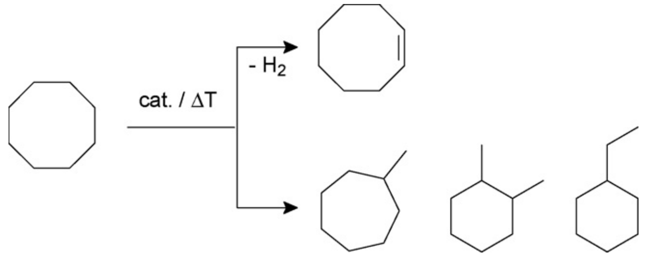
A temperature/TON diagram indicates that most catalysts do no longer have their original compositions at reaction temperatures above 350 °C. Nevertheless the catalysts were active up to 400 °C (Scheme 4). The catalysts produced cyclooctene as the main product.

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.

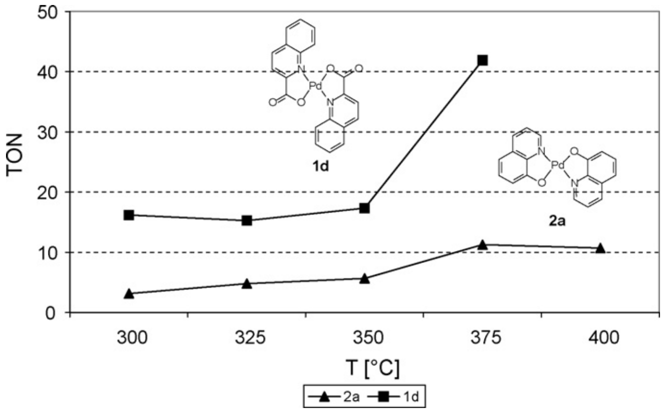
There is a structure–efficiency relationship although the catalysts changed their composition (Scheme 5). The highest turnover numbers of **1b** and **1d** were 18 and 16. A detailed structure–efficiency relationship could not be recognized, the activity differences of catalysts **1b**–**d** and **2a**–**b** 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.