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Ruthenium(II)-PNN pincer complex catalyzed dehydrogenation of benzyl alcohol to ester: A DFT study

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ABSTRACT

The molecular mechanism of the dehydrogenation of primary alcohol to ester catalyzed by the ruthenium(II)-PNN pincer complex Ru(H)(η^2-BH_4)(PNN), [PNN: (2-(di-*tert*-butylphosphinomethyl)-6-(diethlaminomethyl)-pyridine)] has been investigated using density functional theory calculations. The catalytic cycle includes three stages: (stage I) alcohol dehydrogenation to form aldehyde, (stage II) coupling of aldehyde with alcohol to give hemiacetal or ester, and (stage III) hemiacetal dehydrogenation to form ester. Two dehydrogenation reactions occur via the β-H elimination mechanism rather than the bifunctional double hydrogen transfer mechanism, which could be rationalized as the fluxional behavior of the BH_4^- ligand. At the second stage, the coupling reaction requires alcohol or the ruthenium catalyst as mediator. The formation of hemiacetal through the alcohol-mediated pathway is kinetically favorable than the ruthenium catalyst-mediated one, which may be attributed to the smaller steric hindrance when the aldehyde approaches the alcohol moiety in the reaction system. Our results would be helpful for experimental chemists to design more effective transition metal catalysts for dehydrogenation of alcohols.

1. Introduction

Esterification is one of the most fundamental transformations in organic chemistry [1]. Although several methods have been exploited and developed, the search for environmentally friendly, atom-efficient methods which avoid the use of acids, bases, condensing reagents and activators has attracted much attention [2–4]. Among esterification methods, the direct catalytic dehydrogenation of alcohols to esters and molecular hydrogen, without the use of the corresponding acid or acid-derivative, is an attractive approach. However, homogeneous systems capable of thermally catalyzing dehydrogenation of alcohols are relatively rare [5–26]. Recently, Milstein and co-workers prepared a new ruthenium (II) hydrido borohydride complex, Ru(H)(η^2-BH_4)(^{t}Bu-PNN), [^{t}Bu-PNN: (2-(di-*tert*-butylphosphinomethyl)-6-(diethlaminomethyl)-pyridine)] [27]. This ruthenium (II) pincer complex can catalyze the dehydrogenation of secondary alcohols to the corresponding ketones, the dehydrogenative cyclization of diols to lactones, and the dehydrogenative coupling of primary alcohols to esters, accompanied by evolution of molecular hydrogen. It can also catalyze the hydrogenation of nonactivated esters to the corresponding alcohols under relatively mild pressure of hydrogen, neutral and homogeneous conditions. Especially, when a toluene solution of benzyl alcohol and 0.1 mol% Ru(H)(η^2-BH_4)(^{t}Bu-PNN) was refluxed (115 °C) for 24 h in an open system under argon, benzyl benzoate was generated in 99% yield (88% for isolated yield). By Milstein's mechanism, the catalytic dehydrogenation of primary alcohols to esters may proceed through dehydrogenation to the aldehyde followed by (a) a Tischenko-type disproportionation involving the aldehyde or (b) hemiacetal formation from the alcohol and aldehyde followed by the dehydrogenation to the ester. According to the experimental results, Milstein considered that the hemiacetal pathway is likely to be operative [28].

In this work, we will perform density functional theory calculations to explore the mechanistic details of the Ru(H)(η^2-BH_4)(^{t}Bu-PNN)-catalyzed dehydrogenation of benzyl alcohol to benzyl benzoate accompanied by evolution of H_2 (as shown in Scheme 1). The results will provide a general picture on the mechanism of the dehydrogenation of alcohol, and a molecular level picture on how the ruthenium catalyst functions in the dehydrogenation process. The information revealed in this study may be useful to

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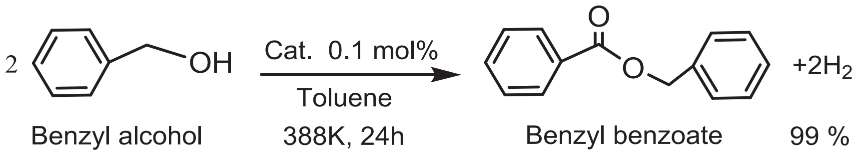
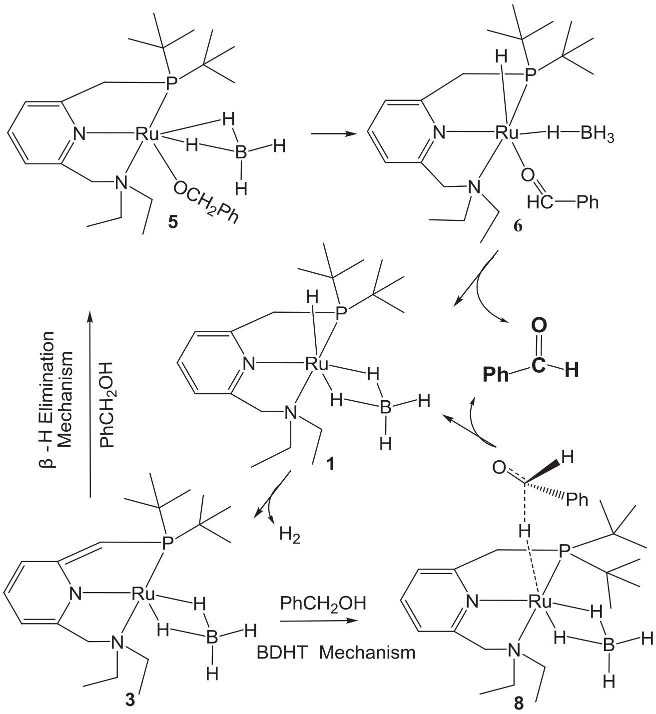


Scheme 1. Catalytic dehydrogenation of benzyl alcohol to benzyl benzoate.



Scheme 2. Benzyl alcohol dehydrogenation via β-H elimination and bifunctional double hydrogen transfer (BDHT).

experimentalists for inventing more effective homogeneous catalysts for dehydrogenation of alcohols.

2. Computational details

All calculations are carried out using the Gaussian03 package [29]. All of the geometries of the reactants, transition states, intermediates and products are fully optimized with the B3LYP density functional method [30,31] in the toluene solvation phase. For the catalyst, relativistic effective core potential (ECP) [32,33] are employed for ruthenium and phosphorus, and a 6-311++G(d, p) basis set is used for other atoms. The basis set for ruthenium is a modified LANL2DZ plus an f-type polarization function [34], in which the two 5p functions of the standard LANL2DZ are replaced by the optimized 5p functions from Couty and Hall [35]. For phosphorus, the standard LANL2DZ augmented by a d-type function with the exponent of 0.387 is used [36]. For all atoms in benzyl alcohol, a 6-311++G(d, p) basis set is utilized. For computational tractability, the phosphine and amine substituents (*tert*-butyl group and ethyl group) of the starting Ru(II) hydrido borohydride complex were replaced by methyl groups.

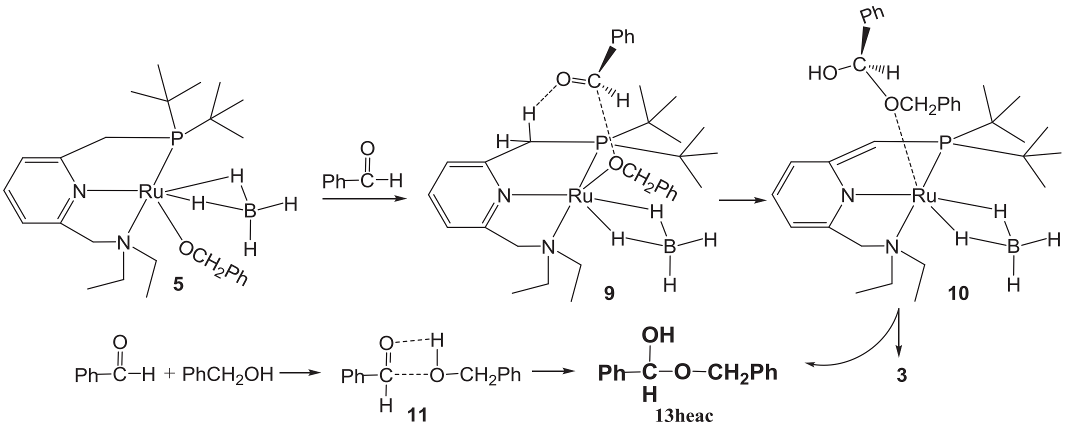
For each stationary point, vibrational frequencies are calculated to obtain zero-point vibrational energies (ZPVE) and verify whether it is a minimum or a transition state. When necessary, intrinsic reaction coordinates (IRC) [37,38] calculations are performed from each transition state to verify whether the reactant and the product are really connected by the transition state. The solvation energy calculations are carried out by using the PCM model [39].

3. Results and discussion

On the basis of the mechanism proposed by Milstein et al., we suggest that the reaction (as shown in Scheme 1) proceeds similarly through three stages: (1) alcohol dehydrogenation to more reactive aldehyde (Scheme 2). (2) coupling reaction of aldehyde with alcohol to form hemiacetal or ester (Schemes 3 and 5). (3) hemiacetal dehydrogenation to ester (Scheme 4). In the following sections, we will discuss the computational details about the three stages. The structures of all stationary points are displayed in Figs. 1, 3, 5 and 7, and their relative free energies are shown in Figs. 2, 4, 6 and 8.

3.1. Alcohol dehydrogenation to form aldehyde

Both β-H elimination and bifunctional double hydrogen transfer (BDHT) mechanisms have been taken into account in the present



Scheme 3. Pathways for the formation of hemiacetal mediated by ruthenium catalyst or by the indirect coupling of aldehyde and alcohol.