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Hydrogenation of biomass-derived levulinic acid to γ-valerolactone catalyzed by PNP-Ir pincer complexes: A computational study

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ABSTRACT

Density functional theory (DFT) calculations were used to study the mechanisms for hydrogenation of biomass-derived levulinic acid (LA) to γ-valerolactone (GVL) catalyzed by PNP-ligated (PNP = 2,6-bis(di-ter-butylphosphinomethyl) pyridine) iridium complexes, $(^{t}BuPNP)IrH_3$, **1**. The transformation proceeds dearomatization/rearomatization including four stages: hydride transfer to give $LA\text{-}H^-$ and dihydride iridium specie $(^{t}BuPNP)IrH_2^+$, methylene proton in the PNP ligand transfer to substrate to form γ-hydroxyvaleric acid (HVA), catalyst regeneration via H_2 splitting, cyclization of HVA to GVL. Compared with the hydrogenation of CO_2 catalyzed by the same complex, herein the rate-limiting step is the hydride transfer step rather than the methylene proton transfer. The calculations show that the hydride transfer step has a significantly higher barrier (21.1 *vs* 5.3 kcal mol^{-1} for the hydrogenation of CO_2). Besides, the cyclization is very easily achieved due to the low barrier. As an alternative pathway, different from the above dearomatization/rearomatization process, a base abstracts a proton from the dihydrogen ligand to form the trihydride iridium with a free energy barrier of 24.6 kcal mol^{-1}. Our results will help in the understanding of the mechanisms of hydrogenation of LA to GVL catalyzed by metal complexes.

1. Introduction

As an ideal alternative to fossil resources, biomass might play a key role in the near future in renewable energy technologies [1]. In recent years, much research has been focused on developing new chemical strategies for the valorization of different biomass components to value-added and/or platform chemicals [2–4]. Especially, as an important biomass derived specie, levulinic acid (LA) can be converted to kinds of fine chemicals, such as γ-valerolactone (GVL), which is widely used as a green solvent, food ingredient, octane booster, and intermediate for fine chemical synthesis [5,6].

In the past few years, much work has been devoted to the development of heterogeneous catalytic system, such as ruthenium or platinum supported on carbon or aluminum oxide, for the synthesis of GVL from LA [7–13]. Not equivalent to the advantages for easily separation/recycling of the heterogeneous catalysts, the homogeneous catalysts can simplify detailed mechanistic studies as well as allow for efficient activity and high level selectivity under relatively mild conditions [14–16]. Previously, several groups have reported the transformation of GVL from LA promoted by homogeneous catalysts such as $RuCl_2(PPh_3)_3$ [17], $Ru(acac)_3/PBu_3$ [18], $Ru(acac)_3P(n\text{-}Oct)_3$ [19], $RuCl_3/PPh_3$ [20], Cp^*IrCl_2/bpy [21] and $Ru(acac)_3$/bis(2-diphenylphosphinoethyl)phenylphosphine [22].

Metal complex with pincer ligands has been applied as an efficient catalyst for the hydrogenation or dehydrogenation reaction [23]. Nozaki et al. reported a PNP-ligated (PNP = 2,6-bis(di-iso-propylphosphinomethyl)pyridine) iridium(III) tri-hydride complex $(^{i}PrPNP)IrH_3$ to achieve the hydrogenation of CO_2, which presented excellent catalytic activity with the TOF and turnover number TON values of 150 000 h^{-1} and 35 000 000, respectively [24]. Then, the mechanism of the catalytic CO_2 hydrogenation reaction using density functional theory (DFT) has been revealed by Ahlquist [25], Yang [26], Hazari [27] and Nozaki [28], respectively, from different perspective. Continuing these successes, metal complex with pincer ligands has also found application in biomass-derived utilization [29]. Knowledge gained from the investigation of the mechanism for metal-complex-promoted the hydrogenation of levulinic acid to γ-valerolactone will help in the design of more efficient metal-complexes [30–48]. Recently, Zhou et al. reported that hydrogenation of LA to GVL in excellent yield (up to 99%) with an extremely high TON (71 000) under relatively mild reaction conditions, which catalyzed by PNP-ligated

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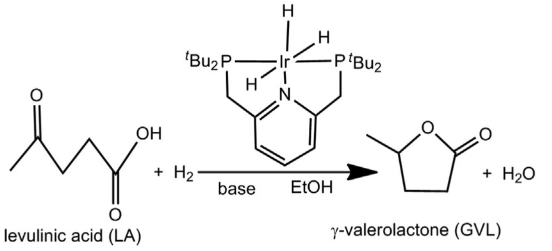

Scheme 1. Hydrogenation reaction of LA to GVL catalyzed by PNP-ligated iridium complex.

(PNP = 2,6-bis(di-ter-butylphosphinomethyl) pyridine) iridium complexes, (^{t}BuPNP)IrH$_3$, **1** [29]. However, the detailed reaction mechanism is still not clear. Herein, we attempt to gain a more detailed understanding of the mechanisms of iridium catalyzed reaction for the catalytic hydrogenation of LA to GVL by employing DFT calculations (Scheme 1).

2. Results and discussion

Hydride transfer. The optimized structure of **1** is shown in Fig. 1, in which a PNP ligand and three hydride coordinated to the Ir center. The first step for the hydrogenation reaction of LA to GVL catalyzed by PNP-ligated iridium complex is depicted in Fig. 2. With the attack of carbon atom in LA molecule to one of the axial hydride in **1**, a hydride is transferred directly from the metal center to the carbon atom through the transition state **TS$_{1,2}$** (21.1 kcal mol^{-1}) for the formation of intermediate **2**. The distances of Ir—H1 in **1**, **TS$_{1,2}$** and **2** are 1.68, 1.99 and 2.09 Å, while the distances of C—H1 in **TS$_{1,2}$** and **2** are 1.40 and 1.28 Å, respectively (Figs. 1 and 3).

Previously, the hydride transfer process for the hydrogenation reaction of CO$_2$ catalyzed by similar PNP-ligated iridium complex had been explored [25,26,28]. All of those calculations shown that the energy barrier of hydride transfer was very low and that the hydride transfer was not the rate-limiting step for the whole reaction [25,26,28]. For the sake of comparison, we also calculated this process and the energy barrier is 5.3 kcal mol^{-1}, which is significantly lower than that of LA to GVL catalyzed by the same complex at the same level of theory. In other word, the hydride transfer step has a significantly higher barrier (21.1 *vs* 5.3 kcal mol^{-1}) for the hydrogenation of CO$_2$), which might effect the activity (turnover number TON values of 71 000 *vs* 35 000 000 in experimental observations). Besides, the distances of Ir—H1 in **TS$_{1,2}$** and **TS$_{1,2'}$** are 1.99

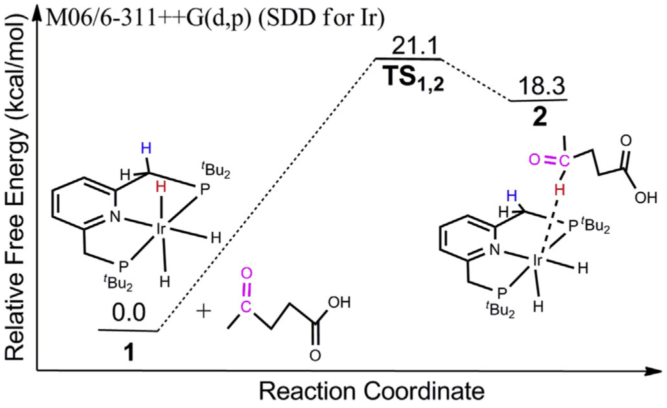

Fig. 2. Free energy profile for hydride transfer process of LA to GVL catalyzed by **1**.

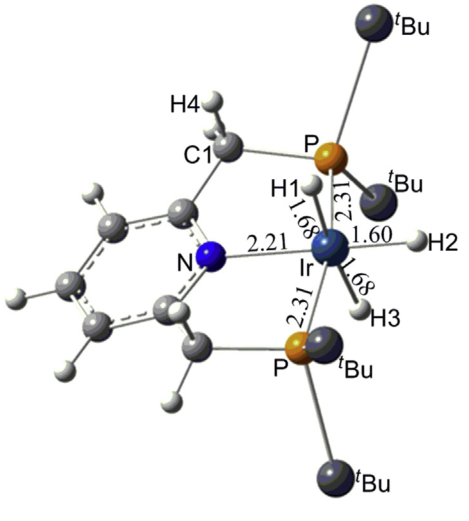

Fig. 1. Optimized structures of the PNP-ligated iridium complex **1**. The distances are in Å.

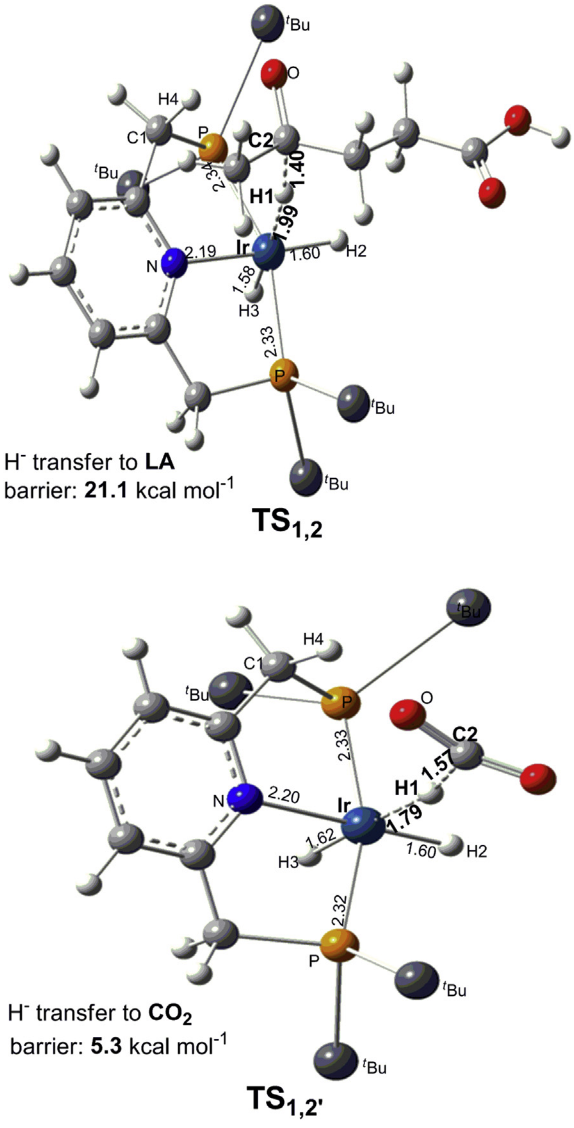

Fig. 3. Comparisons of transition states for hydride transfer process of LA and CO$_2$ catalyzed by **1**, respectively. The distances are in Å.