



Computational insights into the catalytic role of the base promoters in ester hydrogenation with homogeneous non-pincer-based Mn-P,N catalyst



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ABSTRACT

The reaction mechanism of ester hydrogenation catalyzed by a bidentate aminophosphine ligated manganese catalyst was studied by DFT calculations. Particular emphasis was placed on the role of the alkoxide base additives. The presence of such basic promoters as KO^tBu can improve the catalyst activity by lowering the activation barriers of H₂ dissociation as well as the hydrogenation step. The promoting effect of KO^tBu on H₂ activation is much stronger than that of *tert*-butoxides with other alkali metals, which is crucial for the catalyst regeneration from the deactivated Mn-alkoxide species in the resting state.

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1. Introduction

Catalytic reductions of carbonyl derivatives such as ketones, aldehydes, and carboxylic acid derivatives with molecular hydrogen have become a critical synthetic strategy towards the production of a broad scope of bulk and fine chemicals [1–5]. Attractively, catalytic processes employing gaseous H₂ as the reductant principally operate waste-free, and thus are inherently more atom-efficient and environmentally benign compared to the stoichiometric processes employing such reducing agents as lithium aluminium hydride and sodium borohydride currently dominating the pharmaceutical industry [1,6]. While catalytic systems for the reduction of carboxylic acid derivatives historically were based on noble metals [3] (e.g. Ru, Os, and Ir), in recent years attention has shifted towards development of early transition-metal based catalysts such as Fe [7,8], Co [9–11], and Mn [12–15].

Due to its high natural abundance and excellent biocompatibility, manganese is considered an attractive metal for fine-chemical

and pharmaceutical applications as the low toxicity renders quantitative removal of catalytic residues superfluous. Consequently, increased focus of the scientific community has culminated in exceptionally rapid development of a series of highly active Mn-catalysts capable of efficiently reducing particularly challenging carbonyl substrates such as carboxylic acid esters and nitriles [12,13]. This tremendous progress was associated in part with the use of well-established pincer ligand platforms [8,16,17], rather than by the development of novel tailor-made ligands for the chemically distinct Mn(I) systems. This transition, however, does not account for the divergent chemical reactivity of Ru and Mn. The latter, for example differ in the relative stability of metal alkoxide complexes, which are experimentally observed and are often considered off-cycle resting states. Transition metal alkoxides may be considerably more stable than their catalytically active hydride counterparts, as was demonstrated by Gauvin and co-workers in a detailed mechanistic study of acceptorless dehydrogenative coupling (ADC) of alcohols – the microscopic reverse of ester hydrogenation [18].

The often disadvantageous stability of Mn-alkoxides has also been proposed by us [19]. We experimentally observed an unusual dependence of the extent of ester hydrogenation by the Mn catalyst containing bidentate aminophosphine ligand (Mn-P,N **1**) on

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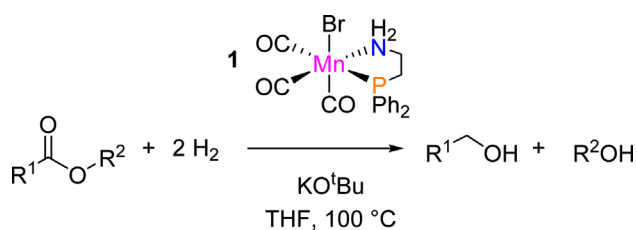
the concentration of KO^tBu base promoter (Scheme 1). This observation led to the proposal of catalyst inhibition by small alcohols formed upon hydrogenation of the ester substrate, ultimately leading to the formation of stable manganese alkoxides [19]. Analogous to the Ru-based systems studied in detail by the groups of Bergens [20] and Morris [21], we hypothesized that the base is required to reactivate the catalytically active hydride species through the base-assisted alkoxide elimination [19]. In conjunction with the large effect of base loading, we experimentally found a strong impact of both the chemical nature of the Lewis acidic alkali metal cation ($K > Na \gg Li$) and the alkoxide fragment ($O^tBu > OEt \gg OMe$) of the basic promoter on the catalytic activity of **1**.

As a separate phenomenon, the Lewis acid promotion is known in homogeneous (de)hydrogenation catalysis [22,23]. Namely, Hartmann and Chen demonstrated experimentally that N–H substitution for N–LA (LA = Li⁺, Na⁺, K⁺) in Noyori-type catalysts is a viable pathway that may assist catalysis by cleavage of molecular H₂ bound to the Ru center with the involvement of an alkoxide anion [22]. Subsequently Dub et al. concluded that the presence of such an O–H functionality (e.g. alcoholic products, protic solvents, traces of water) indeed could reduce hydrogen bond cleavage energies by as much as 40–80 kJ mol⁻¹ [24]. Similarly, it was shown that coordination of potassium to the Ru–N moiety reduced H₂ cleavage barrier by ca. 40 kJ mol⁻¹ [25]. As these detailed works, with few exceptions [26], mainly address noble metal catalyzed ketone hydrogenation, a little is known about the role of base promoters in Mn-catalyzed hydrogenation of esters. With the impact of the base promoter apparently being more critical for Mn catalysis [19] compared to other systems, we aimed here at formulating the rationale behind this effect.

In this work we present a detailed computational study of the mechanism of ester hydrogenation by manganese complexes with bidentate aminophosphine ligands. Particular emphasis is placed on the role of Lewis acid and alkoxide additives that were shown to profoundly impact the catalytic performance. In particular we analyze separately the role of the base at the stage of Mn–P,N complex preactivation and its promoting role within the catalytic cycle for ester hydrogenation (Scheme 2). The results presented not only allow to refine and extend the mechanistic picture postulated earlier for this system but also to create a basis for the discussion of the specific role of base promoters in hydrogenation catalysis by multifunctional catalyst systems.

2. Computational details

All density functional theory (DFT) calculations were performed using the hybrid PBE0 exchange–correlation functional [27] as implemented in Gaussian 09 D.01 program [28]. Our previous studies on homogeneously-catalyzed processes [29,30] have evidenced the high accuracy and predictive power of this methodology for various homogeneously-catalyzed reactions. A recent detailed computational analysis by Leitner and co-workers demonstrates that PBE0 provides the optimal performance in terms of the correctness of the representation of the electronic structure and



Scheme 1. Hydrogenation of ester with a Mn–P,N complex **1**.

reactivity on Mn-containing systems in varying oxidation states [31]. Geometry optimizations were performed with all-electron 6-31G(d) basis set for all atoms, and vibrational analysis was then carried out for all structures at the same level to identify the true nature of the stationary points. All structures corresponding to local minima showed no imaginary frequencies, while transition state (TS) structures were characterized by a single imaginary frequency corresponding to the expected reaction coordinate. Intrinsic reaction coordinate (IRC) approach was employed to examine the connectivity between the transition states and the corresponding minima. The electronic energies were refined by single-point calculations with 6-311+G(d) basis set on all atoms. Bulk solvent effects were accounted for by single-point polarizable continuum model (PCM) corrected at this level of theory using the gas-phase-optimized geometries (THF solvent, $\epsilon = 7.4257$). The reaction (ΔE_{ZPE}) and activation energies (ΔE_{ZPE}^\ddagger) reported in the manuscript were corrected for zero-point energy (ZPE) from the normal-mode frequency analysis. Standard reaction Gibbs free energies (ΔG_{THF}) and activation Gibbs free energies (ΔG_{THF}^\ddagger) in THF solution were computed using the results of the normal-mode analysis within the ideal gas approximation at a pressure of 1 atm and temperature of 373 K. For species in solution, the entropic contribution arising from translational degrees of freedom was computed as 1/2 of that for the isolated gas-phase molecule [32,33].

3. Results and discussion

3.1. Pre-catalyst activation

The direct role of the base promoter in the catalytic ester hydrogenation with **1** and related halide transition metal complexes is to convert them to a catalytically active hydrido species **3** (Scheme 2) capable of sustaining the catalytic cycle. Fig. 1 presents the optimized structures for the reaction intermediates and transition states together with the computed energetics of the elementary reaction steps during the catalyst activation process. The corresponding free energy diagram is shown in Fig. 2. The first step in the catalyst activation sequence is the reaction of **1** with KO^tBu base resulting in an exergonic exchange of the halide ligand in **1** with an O^tBu group to form **2**. To enable the subsequent hydrogenolysis process, a coordination site on the Mn center needs to be liberated. This is achieved via a sequence of rather unfavorable reaction steps involving first the displacement of the O^tBu ligand, which according to the current DFT calculations is accompanied by the deprotonation of the amino-moiety of the bidentate P,N ligand forming **2a** featuring a coordinated HO^tBu molecule. This is followed by the displacement of HO^tBu with an H₂ molecule to form a σ -complex **2c**. The complete reaction sequence is endergonic by 78 kJ mol⁻¹ and proceeds with an apparent free energy barrier of 86 kJ mol⁻¹ ($\Delta G_{373K,THF}^\circ$; $\Delta G_{373K,THF}^\ddagger$). Clearly, the rather weak coordination of molecular H₂ is not sufficient to compensate for the energy losses related to the deprotonation of the P,N ligand and the dissociation of the Mn–O bond during this transformation of the precatalyst **1** to intermediate **2c**. This reaction sequence can therefore be viewed as a pre-activation of both the Mn complex that is followed by a highly exergonic ($\Delta G_{373K,THF}^\circ = -112$ kJ mol⁻¹) and nearly barrierless ($\Delta E^\ddagger = 0$ kJ mol⁻¹; $\Delta G_{373K,THF}^\ddagger = 10$ kJ mol⁻¹) heterolytic splitting of the pre-coordinated H₂ via a 6-membered ring cyclic TS_{2c-2d} to give the Mn-hydrido adduct coordinated to HO^tBu molecule (**2d**). The latter is leaving the reactive ensemble exergonically ($\Delta G_{373K,THF}^\circ = -18$ kJ mol⁻¹) to yield the octahedral complex **3**. The presence of the tert-butanol molecule in the second coordination sphere of Mn is crucial for this activation reaction sequence. First of all, the hydrogen bonding of an alcohol with the amido-moiety in the deprotonated trigonal-bipyramidal Mn–P,N complex (**2b**)

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