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Theoretical investigation on the C—H activation of an enaminone and its coupling reaction with diphenylacetylene to a naphthalene catalyzed by Rh (III) complexes

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ABSTRACT

Direct activation and functionalization of C—H bonds offer a powerful tool to construct various functional molecules such as naphthalenes, which are an important type of aromatic compounds with diverse applications. Catalyzed by $[Cp^*Rh]^{2+}$ complexes, the C—H activation and coupling mechanism of the enaminone (*E*)-3-dimethylamino-1-phenylprop-2-en-1-one with diphenylacetylene to the naphthalene derivative 1-hydroxy-3,4-diphenyl-2-naphthaldehyde were investigated systematically at M062X/6-31G(d,p) level in aqueous solutions. This theoretical model shows that, 1) in the activation of the C—H bond on the benzene ring, the relative energy of the transition state lies at the highest point in the potential energy profiles, so it controls the whole catalytic system; 2) in the energetically most favorable pathway, the activation of the C—H bond on the newly-formed six-membered ring bears the highest energy barrier, so it will be the rate-determining process; 3) in the late-stage hydrolysis, water molecule as both a nucleophile and an electrophile to attack different parts of the naphthalenone; 4) the barrier of two hydrolysis steps is relatively low (58.9 and 82.4 kJ/mol), so they may be faster steps in the whole reaction system.

1. Introduction

Transition-metal-catalyzed activation and selective functionalization of carbon–hydrogen (C—H) bonds have now become a distinguished area in synthetic organic chemistry, and have attracted sustaining attention in recent years [1–7]. Direct activation of C—H bonds is an ideal strategy to construct a variety of functional molecules of more complex structures containing new C—C and carbon–heteroatom bonds such as C—N and C—O [8–11]. However, these omnipresent C—H bonds are chemically inert, and commonly bear low reactivity [12]. The C—H bonds with sp^3 hybridization are generally divided into two main subsets of unreactive and reactive ones [13]. Relative to the aliphatic C—H bonds, in general, reactive sp^3 C—H bonds are linked to sp^2 or sp C atoms, and heteroatoms such as N and O. C(sp^2)—H bonds in alkenes and aromatic compounds are also inclined to be activated and to form cyclic structures.

Naphthalenes are an important type of aromatic compounds with diverse applications [14]. Activated by transition-metal catalyst, direct C(sp^2)—H functionalization of benzene derivatives is a powerful tool for the synthesis of naphthalenes and other poly-fused rings. Recently, Zhu and coworkers [15] reported a Rh^{III}-catalyzed directed C—H functionalization of aromatic enaminones followed by a cyclization reaction with diphenylacetylene to afford naphthalene derivatives. The enaminones with ketone, enamine and even alkene groups are effective and versatile synthons, and can be regarded as an ideal template to investigate C—H functionalization, so a theoretical exploration is urgently needed to elucidate the catalytic mechanism according to the experimental results. In this study, there are two C—H activation processes in this mechanism (Scheme 1): 1) the $[AcO-Rh-Cp^*]^+$ complex abstracts a hydrogen atom from the benzene ring of (*E*)-3-dimethylamino-1-phenylprop-2-en-1-one (**R**) to form a Rh-C bond and release AcOH; 2) after the coupling reaction with diphenylacetylene to form a new six-membered ring, the reduced $[Rh-Cp^*]^+$ species captures another H atom via β-hydride elimination to yield $[Cp^*-Rh-H]^+$ and a naphthalenone **IM9**, which will be hydrolyzed to a naphthalene derivative. The theoretical study can provide at least a helpful complement for the experimental study, and will shed light on the C—H activation and functionalization, thermodynamic properties and coupling mechanisms of aromatic enaminones with alkynes.

2. Computational details

All molecular structures and transition states were located and fully optimized without any constraints with G09 program package [16]. In

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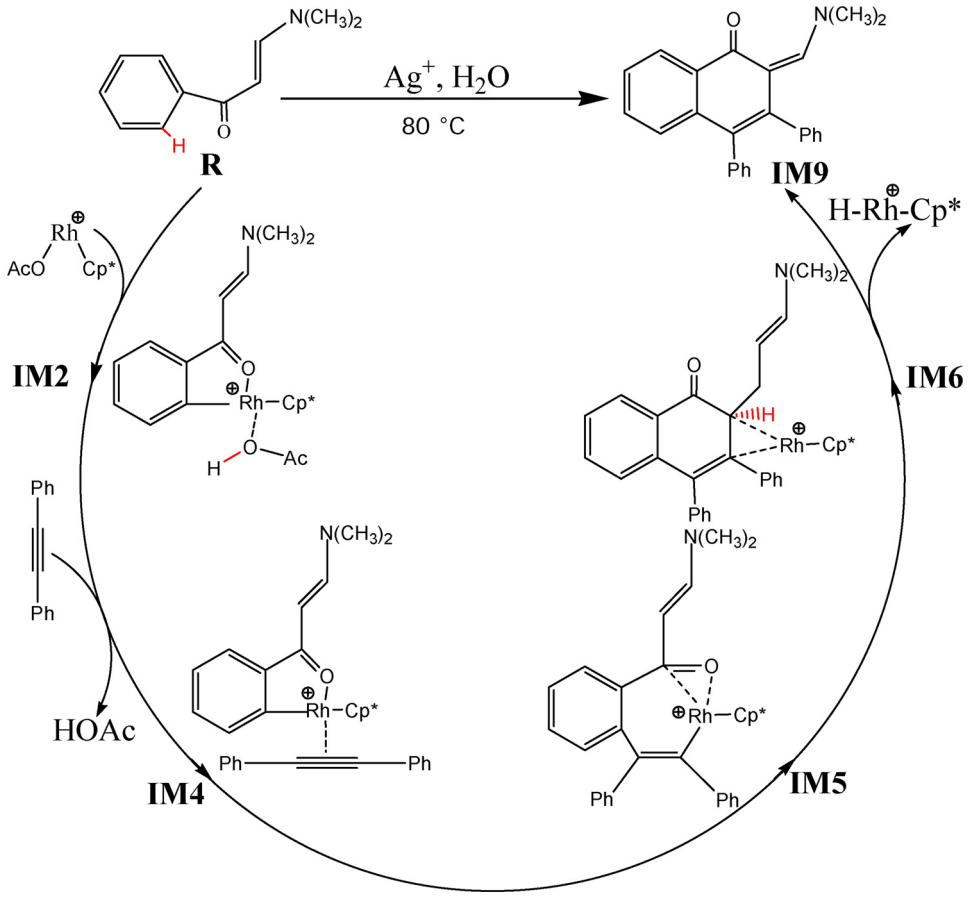

Scheme 1. The two C—H activation processes of **R** mediated by the $[AcO-Rh-Cp^*]^+$ complex, and its subsequent coupling mechanism with diphenylacetylene in the present work.

this catalytic mechanism, the C—H activation and cyclization processes comprise plenty of weak interactions, so the relatively newer M06-2X functional developed by Zhao and Truhlar [17] was employed because this highly parameterized exchange correlation functional can provide accurate information for noncovalent interactions [18–20]. The standard 6–31G(d,p) basis set [21–23] with polarization *d* functions for C, O and N, and *p* functions for H was used through this study, and the Hay and Wadt effective core potentials with a double-ζ valence basis set (LanL2DZ) [24–27] were applied to describe the Rh atom. Frequency calculations were performed to identify whether a stationary point was a local minimum or a transition state, and to calibrate the energies to 298.15 K after thermal correction and zero-point energy correction. To simulate the experimental conditions and to correctly characterize ionic species in aqueous solutions, the Conductor-like Polarizable Continuum Model (CPCM) [28–32] was used to describe bulky water. A transition state was firstly examined by the only imaginary frequency and its vibrational mode, and then its connectivity between the two intermediates was further confirmed by intrinsic reaction coordinate (IRC) scanning [33–38] at the same basis set level. The other settings were by default in G09.

3. Results and discussion

For all singlet-state species in this reaction system, the lowest frequencies and their vibrational mode assignments, as well as the absolute and relative values of electronic and zero-point energies *E*, thermal free energies *G* and thermal enthalpies *H* are listed in table S1 of Supporting Information I. The Cartesian coordinates for all species in the text are listed in Supporting Information II.

3.1. Abstraction of a hydrogen atom from the benzene ring of *R*

Rhodium-catalyzed C(sp^2)—H activation and functionalization is an effective approach to synthetize substituted aromatic compounds. Traditionally, $[(Cp^*RhCl_2)_2]/[Rh(cod)Cl]_2$ and $AgSbF_6$ are used as the precatalysts, and treated with either $Cu(OAc)_2$ or AgOAc to prepare the active catalyst [39,40]. In the experiment of Zhou et al., $[(Cp^*RhCl_2)_2]$ and $AgSbF_6$ were employed to gain the cationic $[AcO-Rh-Cp^*]^+$ catalyst, rather than the neutral catalyst $RhCp^*(OAc)_2$ reported by Han and coworkers[41].

The catalyst $[AcO-Rh-Cp^*]^+$ can active a C(sp^2)—H bond by capturing a hydrogen atom from the benzene ring. The optimized structural parameters and potential energy surface (PES) involved in this C—H activation process are illustrated in Fig. 1. In order to clearly express the orientations of ligands and functional groups, the molecular structures are read from the output files and contain all atoms and groups. For $[AcO-Rh-Cp^*]^+$, AcO^- is bidentately coordinated to $[Rh-Cp^*]^+$, and the monodentately-coordinated complex is less stable by 24.0 kJ/mol, as depicted in Fig. S1 of Supporting Information I. First of all, the O atom of (*E*)-3-dimethylamino-1-phenylprop-2-en-1-one (**R**) coordinates to the Rh vacancy of the catalyst to generate **IM1**, decreasing the Gibbs free energy by 11.9 kJ/mol. Owing to the complexation of the Cp* ring, Fig. S2 of Supporting Information I proves that the lowest-lying singlet $[AcO-Rh-Cp^*]^+$ and **IM1** are much lower than their corresponding triplet and quintuplet ones, so the Rh complexes in this work adopt low-spin states. In **IM1**, the bond lengths of Rh with the activating H atom and the O atom of **R** are 2.622 and 2.155 Å, respectively. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of **IM1** illustrate that, the Rh atom is coordinatively unsaturated and may form σ bonds or π