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Key mechanistic insights into the intramolecular C-H bond amination and double bond aziridination in sulfamate esters catalyzed by dirhodium tetracarboxylate complexes

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ABSTRACT

Density Functional Theory was used to study the mechanisms of intramolecular C-H amination and olefin aziridination reactions of a variety of sulfamate esters. Particular emphasis is placed on the mechanism and factors governing amination of primary, secondary, tertiary and benzylic C-H bonds, the competition between tertiary and benzylic C-H amination, and the competition between allylic C-H amination and olefin aziridination. In these studies we used three different dirhodium paddlewheel catalysts, such as model $(H_2O)Rh_2(O_2CH)_4$ (**I**), $(H_2O)Rh_2(AcO)_4$ (**II**), and $(H_2O)Rh_2(esp)_2$ (**III**). In general, we found that all catalysts have a diamagnetic closed shell singlet state with a single Rh-Rh σ-bond. Active catalytic species in the studied amination reactions are triplet state dirhodium-nitrene complexes with the Rh—Rh single bond and Rh-N double bond (with one σ-bond and two "one-electron π-bonds"). From the active nitrenoid species, the C-H bond amination proceeds via triplet-to-singlet surface crossing and singlet state concerted C-H insertion mechanism. The calculated energy barriers correlate with the trend in homolytic bond dissociation energy of the activated C-H bonds. With the allylic substrate, the competing C=C double bond aziridination follows a stepwise pathway involving the formation of radical intermediate and radical coupling to produce singlet aziridination product. However, the allylic C-H bond amination occurs with a lower barrier which is consistent with experimental product distributions.

1. Introduction

Nitrogen-containing functional groups are ubiquitous in natural and pharmaceutical products, which makes C-N bond formation a main target in organic synthesis [1,2]. Direct C-H bond and an aliphatic C=C double bond functionalization through transition metal catalysis are appealing approaches to accomplish this important goal [3-6]. The use of C—H amination and C=C bond aziridination methods allow for direct access to the desired C—N functionality in a vast range of hydrocarbons and are cost-effective and environmentally friendly. Currently, there exist a number of examples of such processes utilizing various complexes of rhodium [1-9], ruthenium [1,2,10,11], cobalt [2,12], iron [2,13], copper [2,14], and other metals [2,15,16]. Among these complexes, dirhodium paddlewheel complexes appear to be the most efficient. The structural motifs of dirhodium paddlewheel complexes and their stability during catalyst turnover allow selective functionalization of various C—H and C=C double bonds [2,4-8,17]. Indeed, a given substrate can possess different C—H centers and a competition between them during functionalization might arise. Common C—H bonds are terminal (primary), secondary, tertiary, and benzylic C-H bonds. It is expected that the degree of reactivity of these types of C—H bonds is different with tertiary and benzylic C-H bonds being the weakest based on homolytic bond dissociation energy. The positioning of an allylic C-H bond adjacent to a double bond imposes additional practical and mechanistic complexity because of competition between the C—H bond amination and double bond aziridination under essentially the same reaction conditions. Generally, such reactions result in undesirable mixtures of several products with low or no chemoselectivity and the product distribution is strongly catalyst- and substrate substrate-dependent [18-21].

Thus, a deeper understanding of mechanisms and governing factors for selective amination of various C-H bonds, as well as C=C double bond in the presence of allylic C-H bond, is absolutely vital for designing selective transition metal catalysts for C-H and C=C bond amination. Therefore, one of goals of this paper is to elucidate

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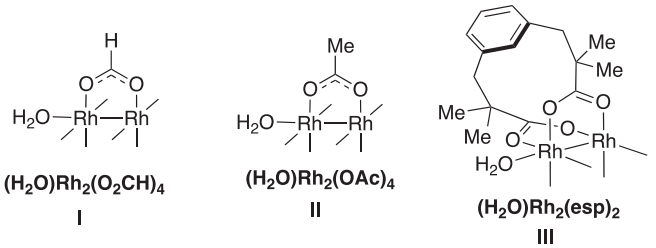
the mechanisms and controlling factors for intramolecular amination of various (primary, secondary, tertiary, and benzylic, eq. (1) in Scheme 1) C-H bonds in sulfamate esters catalyzed by dirhodium tetracarboxylates to generate oxathiazinanes, which was developed by Du Bois and co-workers.[19a,c-e,g-j,21] Another goal is to understand the mechanisms and controlling factors of selectivity between intramolecular C-H bond amination and C=C double bond aziridination for allylic substrates. For this purpose, we study these processes for olefin sulfamate esters catalyzed by dirhodium tetracarboxylate catalysts (Eq. (2), in Scheme 1). In order to better understand reasons and impact of nature of dirhodium catalyst to selective tertiary and benzylic C-H amination we also study reaction (3) (see Scheme 1 for Eqs. (1),(2) and (3)), which was previously reported. [11,19l].

In literature, several dirhodium catalysts were used to catalyze the targeted transformations. In earlier publications the simplest dirhodium tetracarboxylate $Rh_2(OAc)_4$ catalysts (see Scheme 2) has been widely employed.[19f,g,j] Later, the $Rh_2(esp)_2$ catalyst (where esp = α, α, α′, α′−tetramethyl-1,3-benzenedipropanoate) as well as $Rh_2(OAc)_4$ catalyst [19e,h,j] is most extensively used.

Therefore, here, we use three different catalysts (Scheme 2): the experimentally relevant catalysts $(H_2O)Rh_2(OAc)_4$ and $(H_2O)Rh_2(esp)_2$, and the $(H_2O)Rh_2(O_2CH)_4$ model catalyst that is widely employed by theoreticians (see discussion below). We expect that comparison of the calculated data for real catalysts $(H_2O)Rh_2(OAc)_4$ and $(H_2O)Rh_2(esp)_2$, with those model catalyst $(H_2O)Rh_2(O_2CH)_4$ will allow us validate the applicability of the model extensively used in previous studies.

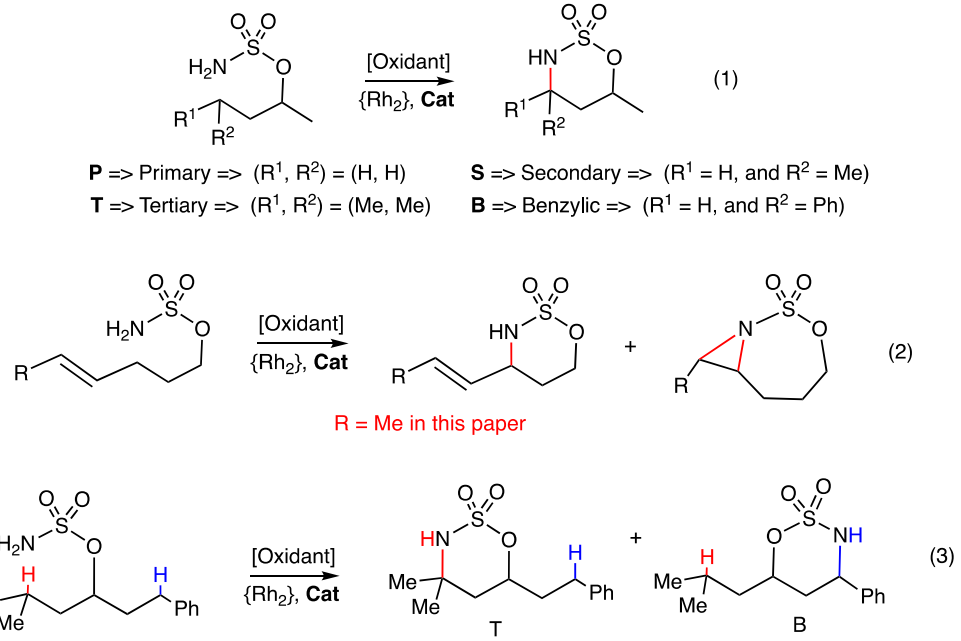
As mentioned above the reactions (1), (2) and (3) (see Scheme 1), previously were subject of several computational analyses. Zhao and co-workers [22] used the density functional approach and studied mechanism of the $Rh_2(O_2CH)_4$, Rh_2(*N*-methylformamide)$_4$ and Rh_2(*S*-nap)$_4$ catalyzed intramolecular benzylic C-H amination of 3-phenyl-propylsulfamate. The authors have shown that C−H amination starts from the Rh_2-nitrene intermediate with lower-lying singlet and triplet electronic states. In general, singlet state process occurs via a concerted C-H insertion mechanism, while triplet state process may proceed via a stepwise pathway involving (a) intramolecular H-abstraction to generate a diradical intermediate, and (b) radical recombination to form final product. In a subsequent paper, Zhao and coworkers extended their study to elucidate the mechanism of the intramolecular allylic C−H amination and double bond aziridination in 4-pentenylsulfamate [23]. In this study, the authors used model catalysts $Rh_2(OAc)_4$, $Rh_2(NHCOCF_3)_4$ and $Rh_2(NCH_3CHO)_4$, and found: (a) the singlet concerted, highly asynchronous pathway for the C-H amination, and triplet stepwise pathway for the alkene aziridination reaction, and (b) the $Rh_2(OAc)_4$ and $Rh_2(CHCOCF_3)_4$ catalysts show similar reactivity patterns. In general, for all three catalysts, C-H amination is found to be more favorable than double bond aziridination.



Scheme 2. Schematic representation of the used $(H_2O)Rh_2(O_2CH)_4$, $(H_2O)Rh_2(OAc)_4$ and $(H_2O)Rh_2(esp)_2$ catalysts in this study.

Just recently, Wang and co-workers [24] have reported a comparative study of inter- and intramolecular (reaction 3, in Scheme 1) C−H amination by the $Rh_2(esp)_2$ catalyst. The authors have concluded that: (a) inter- and intra-molecular C−H bond amination proceed via different spin-state pathways, and the difference in the spin states is a reason for the observed benzylic-to-tertiary site selectivity switch; (b) the singlet- and triplet-state mechanisms are concerted hydride-transfer and stepwise H-atom abstraction processes, respectively, and (c) for the intramolecular C−H amination, the singlet-state concerted mechanism is dominant.

Thus, the previous computational studies on the reactions



Scheme 1. Schematic presentation of various C−H bond amination in sulfamate ester (Eq. (1)), the allylic C−H bond amination and C=C double bond aziridination (Eq. (2)), and selective tertiary and benzylic C-H amination (Eq. (3)), catalyzed by different dirhodium catalysts. Selected reactions previously were reported by Du Bois and co-workers. [19f,g,j, 21].