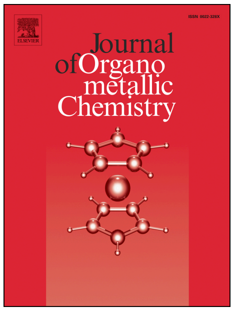

Comparative computational study on C-C/C-N/C-Br bond formations in Rh(III)-catalyzed C-H functionalizations: Stepwise versus concerted mechanisms

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Comparative computational study on C-C/C-N/C-Br bond formations in Rh(III)-catalyzed C-H functionalizations: stepwise versus concerted mechanisms

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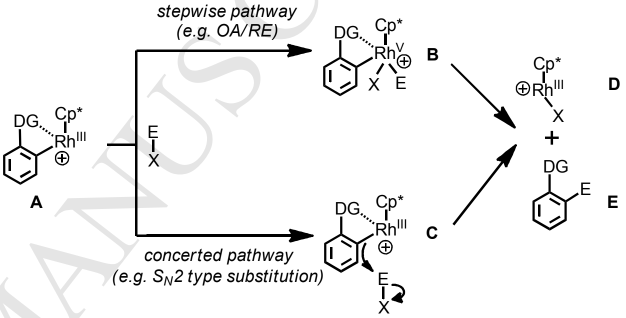
Supporting Information Placeholder

ABSTRACT: In this study, based on DFT calculations, we systematically investigated the mechanisms of Rh(III)-catalyzed C-H ortho-functionalizations of arenes. For C-C, C-N, and C-Br bond formations in four reactions, two types of mechanisms, i.e., stepwise pathway and concerted pathway, are compared. Our DFT theoretical modelings indicate that the mechanisms are highly system dependent. For different types of C-C/C-N/C-Br bond formations, either stepwise or concerted pathways can be preferred kinetically. This preference can also be affected by the substrate/reagent, as shown in C-H amidation reactions. The mechanistic variation of the Rh(III)-catalyzed C-H functionalizations revealed in this work demonstrates high complexity of these organic transformations.

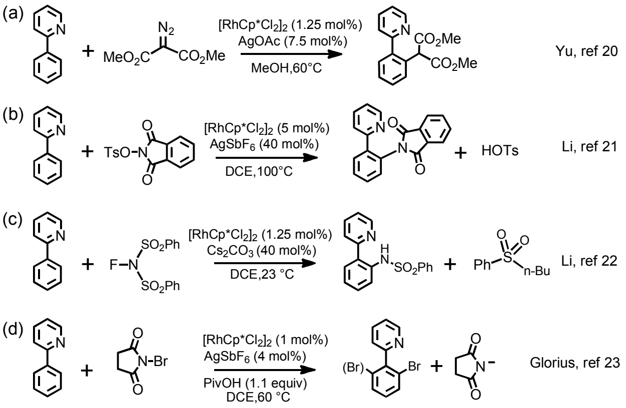
KEYWORDS: *C-H functionalization, Rhodium, DFT calculation, Reaction mechanism, Stepwise pathway, Concerted pathway*

1. INTRODUCTION

In the last ten years, C(sp^2)-H functionalization reactions by Rh(III) catalysts bearing cyclopentadienyl (Cp*) type ligands have witnessed great developments [1-7], through which high-yielding, versatile, and practical ortho-functionlizations of arenes have been achieved. In most of these C(sp^2)-H functionalization reactions, it is considered that the common initial C-H bond activation generating Rh-C bond in cyclometalated intermediate **A** is followed by various C-C and C-heteroatom formation processes to render the final products (Scheme 1). Concerning this key second step for a variety of C-E (E = carbon or heteroatom) formation processes from Rh-C cyclometalated intermediate, there are generally two possible reaction pathways. One is a stepwise mechanism of C-E bond formation via e.g. sequential oxidative addition (OA) and reductive elimination (RE) process that involves high-valent Rh(V) intermediate; the other is the concerted pathway of e.g. S_N2 type substitution in which Rh remains in its +3 oxidation state throughout the whole reaction (Scheme 1). Therefore, it is crucial to know whether the high-valent Rh^V intermediate is involved in these reactions. [8]



Scheme 1. **Two Possible Reaction Pathways Following Cyclometalation for Rh(III)-catalyzed C-H functionalization**



Scheme 2. Typical Intermolecular C-H functionalization Reactions Catalyzed by Rh(III)

Despite that there is currently no direct experimental evidence to support the existence of Rh(V) intermediates [9], a few recent theoretical studies have suggested that Rh(V) intermediates could be formed by oxidative addition in some cases [10-19]. However, these theoretical studies for specific reactions from different authors were often done at different computational levels, which causes difficulty in making a systematic comparison between different reactions. In this work, to systematically explore the preferred pathway of C-E formation in C(sp^2)-H functionalization reactions by Cp*Rh(III) catalysts, we selected four typical intermolecular C-H activation reactions (Scheme 2) [20-23]. For these C-C/C-N/C-Br bond formation processes, density functional theory (DFT) calculations are performed herein to compare the con-