



DFT study of the single electron transfer mechanisms in Ni-Catalyzed reductive cross-coupling of aryl bromide and alkyl bromide



Qinghua Ren^{*}, Feng Jiang, Hegui Gong

Department of Chemistry, Shanghai University, 99 Shangda Road, Shanghai 200444, China

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ABSTRACT

Ni-catalyzed reductive cross-coupling reactions of electrophilic reagents provide an important method to form C–C bonds. The present study explored several single electron transfer mechanisms for Ni-catalyzed reductive cross-coupling of aryl bromide and secondary alkyl bromide using Density Functional Theory (DFT) calculations. The results showed that two of the proposed mechanisms were feasible. One was a six-step catalytic cycle including oxidative addition, reduction, radical production, radical addition, reductive elimination and catalyst regeneration. The other was a five-step mechanism involving radical production, reduction, oxidative addition, radical addition, and reductive elimination. The rate-limiting step for both mechanisms was the radical addition step with the energy barrier of 10.42 kcal/mol. All DFT calculations were implemented in the gas phase.

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Introduction

Transition metal catalyzed reductive cross-coupling reaction provides a powerful method for the formation of carbon–carbon bonds [1–8]. Compared to the traditional cross-coupling reactions such as Suzuki [9–13], Kumada [14–17], and Negishi [18–21] reactions, this method can effectively avoid dealing with the carbon nucleophiles, most of which are sensitive to the environment and generally are not commercially available [22,23]. In recent years, the reductive cross-coupling reaction has been extensively studied experimentally. For example, C. Gosimini et al. studied Co-catalyzed reductive cross-coupling between alkyl halides and allylic acetates or carbonates [1]; Daniel J. Weix et al. reported Ni-catalyzed reductive alkylation of aryl halides [4,6]; Gong et al. investigated Ni-catalyzed cross-coupling of alkyl halides with aryl acid chlorides [7].

Some mechanistic investigations for these kinds of catalytic reactions have also been reported. For example, C. Gosimini et al. explored the mechanism of Co-catalyzed formation of biphenyl using Density Functional Theory (DFT) calculations and confirmed that Co^I was favored as the active catalysts [24]. Our group reported theoretical investigation of the homo-coupling mechanisms of the biphenyl formation in Ni-catalyzed reductive cross-coupling

system and found that the triplet Ni⁰ active catalyst was favored over the singlet Ni⁰ and the Ni^I catalyst [25]. Daniel J. Weix et al. discussed the proposed mechanisms of Ni-catalyzed reductive cross-coupling between aryl halides and alkyl halides using experimental methods [26].

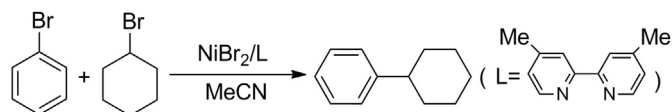
However, until now, no theoretical investigation of Ni-catalyzed reductive cross-coupling of aryl bromide and alkyl bromide using DFT calculations has yet been reported. The present study was the first one to explore the detailed mechanisms of Ni-catalyzed reductive cross-coupling between aryl halide and secondary alkyl halide using DFT calculations, in order to determine the favored catalytic cycle. We have studied several single electron transfer mechanisms and the concerted mechanisms. We hope to clarify the questions which catalytic cycle is feasible and which step is the rate-determining step. Answers to these questions will improve the understanding of these kinds of Ni-catalyzed reductive cross-coupling reactions.

Computational details

All calculations were carried out using DFT with the B3LYP hybrid functional [27–31]. The 6-31g* basis set was used for all atoms (C,H,N,Br and Ni) [32,33], and the gas phase geometries of all intermediates and transition states were fully optimized without any symmetry restriction, following the vibrational frequencies analysis to ensure that the local minima had zero imaginary frequencies and the transition state had exactly one. All DFT

^{*} Corresponding author. Tel.: +86 21 66132404; fax: +86 21 66134594.

E-mail address: qinghua.ren@shu.edu.cn (Q. Ren).



Scheme 1. Model reaction of Bromobenzene (R_1) and Cyclohexyl bromide (R_2).

calculations were implemented in the gas phase using the Gaussian 03 program [34].

Results and discussion

Model reaction

The model reaction based on Gong's work [35] was shown in Scheme 1. Bromobenzene (R_1) and Cyclohexyl bromide (R_2) were chosen as the substrates, and $NiBr_2$ was used as the catalyst precursor. The solvent was MeCN and 4,4'-di-methyl-2,2'-bipyridine (L) was used as the ligand. Here, only the stable chair conformation for the molecular structure of R_2 was considered.

Proposed mechanisms

In the last few decades, mechanistic investigations in transition metal catalyzed cross-coupling reactions have been widely reported [36,37]. Based on the previous studies, we gave several mechanistic proposals including four paths in two cycles, which were shown in Scheme 2. For Path I and II in Cycle A, the active catalyst initially combined with the alkyl bromide, while the active catalyst firstly connected with the aryl bromide for Path III and IV in Cycle B. Here the triplet Ni^0 catalyst was favored over the singlet Ni^0 and the Ni^I catalysts [25], so that the singlet Ni^0 and Ni^I acting as the active catalysts will not be discussed (see their optimized structures in Figure S8 in the supporting information).

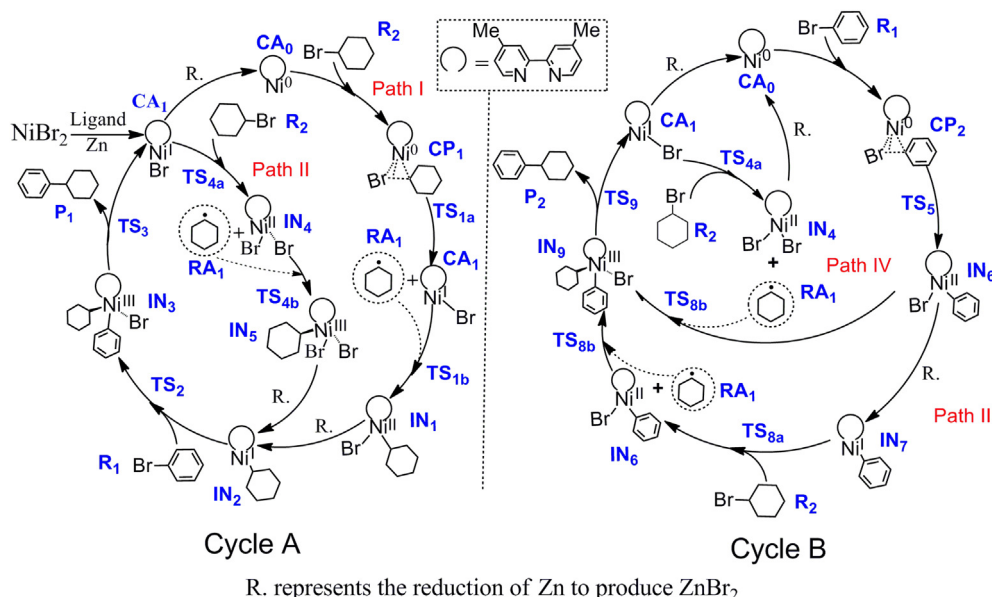
Path I in cycle A: Ni^0 catalyst initially combines with alkyl bromide

In the previous studies, J. K. Kochi et al. studied the mechanism of the reaction between Ni^0 complexes and aromatic halides. They

confirmed that the reaction mechanism included a single electron transfer process in which the metal complexes acted as the electron donor and the organic halide was the electron acceptor [38]. Similarly, James H. Espenson et al. investigated the mechanism of organonickel complexes catalyzed carbon–carbon bond formation and also indicated the existence of radicals [39]. Recently, Fu et al. explored the mechanisms of Ni-catalyzed alkyl–alkyl Suzuki cross-coupling using DFT calculations and found a single electron transfer mechanism catalyzed by the active Ni^0 complexes [40]. Based on the above results, a proposed mechanism named as Path I which involved a single electron transfer process in the oxidative addition step was explored, where the overall catalytic cycle was shown in Cycle A of Scheme 2.

The Gibbs free energy profile in the gas phase for the overall catalytic cycle of path I was shown in Fig. 1. It can be seen that the energy barrier of the first oxidative addition (TS_{1b}) is 7.66 kcal/mol. In the step, the radical RA_1 attacks CA_1 to form the intermediate IN_{1t} . However, the energy barrier of the step producing the radical RA_1 is very slight (only 0.21 kcal/mol for TS_{1a}). The possible reason is that the formation of the complexes CP_1 (CP_{1t} in Fig. 1 means the favored triplet Ni^0 complex) makes the C–Br bond of R_2 weakened and easily broken (The C–Br bond of R_2 is 2.00 Å, but it is 2.11 Å in CP_{1t} , which can be seen in the optimized structures shown in Figure S3 in the supporting information). For the second oxidative addition step, the energy barrier of the concerted transition state TS_2 is 8.88 kcal/mol. No radical mechanism could be found in this step. Similarly, Diego J. Cardenas et al. [41] reported Ni-catalyzed cross-coupling of alkyl zinc halides and aryl halides, and also only gave the concerted transition state in the oxidative addition of Ni^I complexes and aryl halides. Our group had studied the mechanism of Ni-catalyzed reductive homocoupling of aryl halides using DFT calculations and also did not find the radical mechanism for this step [25].

The rate-determining step of the overall catalytic cycle in path I is the reductive elimination step. Its energy barrier (TS_3) is 12.76 kcal/mol, which is different from our previous work on Ni-catalyzed homocoupling of aryl halides to form biphenyl where the reductive elimination process was easy to happen and the energy barrier was only 2.37 kcal/mol [25]. This is probably because of the steric effect of the non-planar structure of cyclohexyl in the



Scheme 2. Proposed mechanisms of Ni-catalyzed reductive cross-coupling of aryl halide and alkyl halide.

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