Theoretical description for the Rh(I)-catalyzed borylation mechanism of a typical aryl cyanide

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ABSTRACT

A recent experimental study by Tobisu et al. (J. Am. Chem. Soc. 2012, 134, 115–118.) reported a new type of catalytic borylation reactions, the Rh-catalytic reaction of aryl cyanides with diboron to afford aryl-boronic acids. To better understand the borylation mechanism at the molecular level, this work provides a theoretical description for the elementary steps of the reaction of a typical aryl cyanide with diboron in the presence of a rhodium catalyst [RhCl(cod)]$_2$ with the aid of DFT calculations. It is found that i) the catalytically active species is the Rh–B complex rather than the Rh–Cl one, ii) the Rh–Ar intermediate is formed through the iminoacyl species rather than the iminylrhodium species previously proposed by Tobisu et al., and iii) the structures of iminoacyl and boryl isocyanide species are also disagreement with those experimental studied by Tobisu et al. Calculated results show a clear mechanistic picture of the catalytic borylation reaction of the aryl cyanide.

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1. Introduction

Arylboronic acids and their derivatives play a crucial role in organic synthesis [1–3], due to their unique reactivity in a variety of reactions, including Petasis–Borono Mannich reactions [4], Chan–Lam coupling [5], conjugate addition reactions [6], and cross-coupling reactions to construct C–C bonds [7]. Functional-group-tolerant catalytic methods for their synthesis have attracted considerable attention [8–10]. Using hydroboron or diboron reagents, several research groups have successfully carried out catalytic borylation reactions of aromatic C-X bonds in the presence of palladium [11–13], copper [14], or nickel [15] catalysts and of aromatic C–H bonds in the presence of rhodium or iridium catalysts [16,17]. More recently, Tobisu's group reported the third type of catalytic borylation reactions in which the C–CN bonds in a range of aryl cyanides were borylated in the presence of a rhodium catalyst [RhCl(cod)]$_2$ [18]. Scheme 1 shows a representative example of these catalyzed borylation reactions, where the reaction of nitrile **1** with diboron reagent **2** in the presence of a base and

PPh$_3$ ligand affords borylated product **3** with yield of 55% and boryl cyanide species **4**.

The finding of Tobisu's group provides a new strategy not only for synthesizing arylboronic acids but also for cleaving C–CN bonds whose activations generally need the presence of a silymetal complex or Ni(0) [19–23]. Related transformations of C–CN bonds into C–Si [24,25], C–H [26,27], and C–C [25,28–31] bonds in the presence of rhodium catalysts and organosilicon reagents and palladium and nickel catalysts have also been reported by groups of Tobisu, Nishihara and Jacobsen. In these reactions of rhodium catalysts and organosilicon reagents, a silylrhodium complex was postulated to be the catalytically active species.

Tobisu et al. [18] have proposed a possible pathway for the Rh(I)-catalyzed borylation of aryl cyanides (Scheme 2), and to understand the relevant mechanism, Fu et al. [32] and Tobisu et al. [33] have also performed density functional theory (DFT) calculations for a representative system containing the Xantphos ligand, which have provided fundamental insights into the overall reaction pathways and some of the elementary steps. However, our understanding on the new type of borylation reactions is still not complete. In this work, the Rh(I)-catalyzed borylation of aryl cyanides using PPh$_3$ ligand shown in Scheme 1 was selected as an example for our study. We aim to show a clear mechanistic picture of the catalytic borylation reaction of the aryl cyanide.
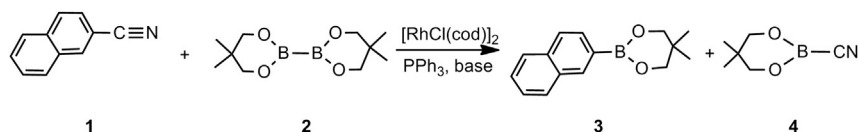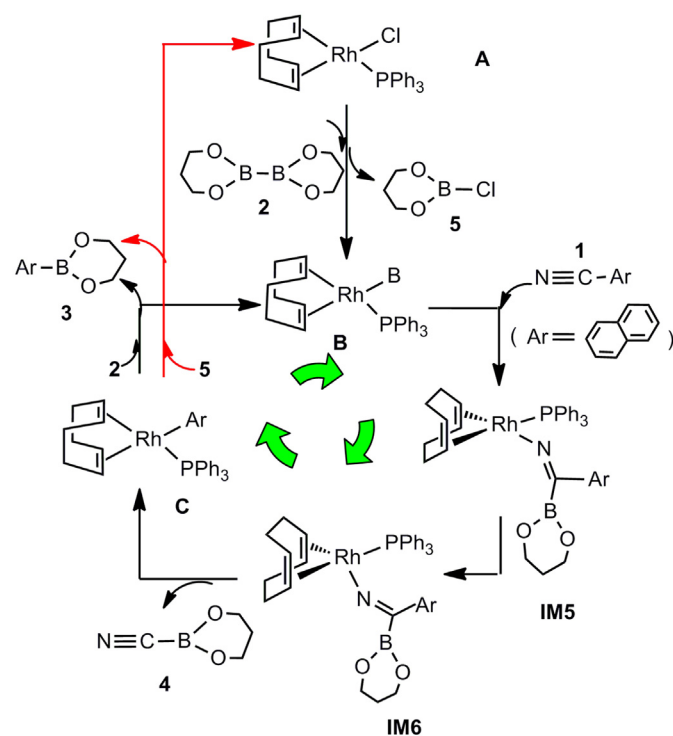
Scheme 1. Catalytic borylation reaction of a representative aryl nitrile reported by Tobisu et al. [18].

1.1. Computational details

Molecular geometries of all the complexes were fully optimized in the framework of density functional theory (DFT) [34–37]. The B3LYP functional is chosen for our calculations, and the LanL2DZ basis set [38] was used for Rh, Cl and P atoms and the 6-31G [39] basis set for other atoms. Polarization functions were added for all the atoms [C($\zeta_d = 0.8$), O($\zeta_d = 0.8$), N($\zeta_d = 0.8$), B($\zeta_d = 0.8$), H($\zeta_p = 0.11$), Cl($\zeta_d = 0.514$) and Rh($\zeta_f = 0.075$)]. Frequency calculations at the same level of theory were also performed to identify all the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency). The intrinsic reaction coordinate (IRC) analysis was carried out to confirm that all stationary points are smoothly connected to each other.

According to results of Norrby et al. [40], dispersion effects are very crucial of metal-phosphine dissociation. Therefore, the dispersion-corrected DFT calculations have been carried out using the B3LYP-D functional and all relative energies reported in this study have included the dispersion energy corrections. All calculations were performed with the GAUSSIAN 09 packages [41]. Cartesian coordinates of all species involved in this study are given in the supporting information.

To reduce the computer cost, the methyl groups in the diboron reagent (**2** in Scheme 1) were replaced by hydrogen atoms. The errors resulted from this simplification are expected to be unimportant because the methyl groups do not directly participate in reaction. Moreover, small systematic errors resulted from the simplification can be mostly counteracted in the relative energy calculations.

## 2. Results and discussion

2.1. Dissociation of [RhCl(cod)]₂

As shown in Scheme 1, the catalyst [RhCl(cod)]₂ used in the experiment is cyclooctadiene rhodium chloride dimer, which is a halide-bridged complex with the rhodium atoms in a square-planar configuration [42]. It is believed that in the catalytic reaction shown by Scheme 1, the dimeric catalyst firstly decomposes into its monomer [RhCl(cod)] (denoted as **A** in Scheme 2), a catalytic active species, to initiate the reaction. The direct unimolecular dissociation of [RhCl(cod)]₂ is calculated to be an endothermic process, involving an energy demand of 27.8 kcal/mol (equ. 1 in Scheme 3). However, with the assistance of PPh₃ ligand, one of phosphine ligands used in the experiment of Tobisu's group, the dissociation of [RhCl(cod)]₂ was found to become an almost exothermic process (equ. 2 in Scheme 3), indicating PPh₃ ligand plays a role of stabilizing RhCl(cod) monomer by forming RhCl(cod)-PPh₃ complex (**A′**).

3. Coordination of nitrile 1 to the Rh center

In a catalytic reaction, coordination of substrates to catalyst is an essential and initial step. Once the monomeric species RhCl(cod) (**A**) is formed, the subsequent step is the coordination of either nitrile **1** or diboron **2** to the metal center. We first study the former case, i.e. the coordination of nitrile **1** to the metal center. If nitrile **1** approachs the Rh center, the reaction will initiate from Rh(I) inserting into Ar—CN bond through transition state **TS₁** to form **IM1** (Fig. 1). Our calculations show that this process is endothermic by 40.1 kcal/mol and involves a barrier as high as 58.0 kcal/mol, implying an unaccessible pathway under thermal reaction conditions. Thus it seems that the catalytic reaction can not start via coordination of nitrile **1** to the catalyst.

4. Coordination of diboron regent to the Rh center and the formation of Rh—B species

Our attention now turns to the reaction starting from the

Scheme 2. Catalytic borylation mechanism of nitrile **1** proposed by Tobisu et al. [18].
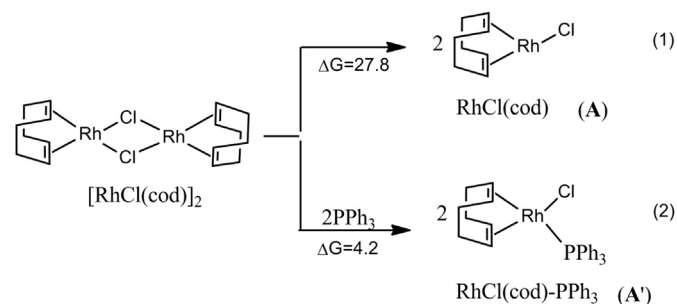
Scheme 3. Calculated free energy changes (in kcal/mol) for the dissociations of [RhCl(cod)]₂ with and without the assistance of PPh₃ ligand.