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Mechanistic Insight into the Nickel-Catalyzed Cross-Coupling of Aryl Phosphates with Arylboronic Acids: Potassium Phosphate is Not a Spectator Base but is Involved in the Transmetalation Step in the Suzuki–Miyaura Reaction

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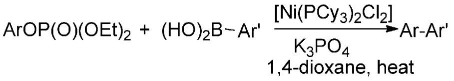
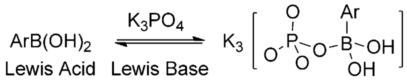
Carbon–carbon (C–C) and carbon–heteroatom (C–X) bond-forming reactions are highly important for the construction of structurally sophisticated compounds in the synthesis of functional molecules, such as organic electronic materials and biologically active compounds.[1] Among these reactions, nickel-catalyzed Suzuki–Miyaura cross-coupling (SMC) reactions have attracted increasing attention for their high efficiency and inexpensive catalyst systems.[2] In most of these nickel-catalyzed SMC reactions, an appropriate and excessive base is particularly important. However, its function in the reaction is controversial.[2r,3] Recently, we reported the nickel-catalyzed cross-coupling of aryl phosphates with arylboronic acids to give a variety of biaryl compounds (Scheme 1).[2q] In an initial study, we found that different bases significantly affected this reaction. For example, when 2-naphthyl phosphates and phenylboronic acid were chosen as the model substrates, a screening of various bases showed that potassium phosphate (4.5 equiv) was the most-effective base to generate the desired product, 2-phenylnaphthalene (93 %). No obvious change in yield was observed when the loading of K_3PO_4 was increased to 5.0 equivalents. Note that this reaction performed well with an even stronger base, such as KOH (4.5 equiv, 80 % yield). Interestingly, in the reaction system, aryl phosphates could be dehydrated to form P–O$^-$ complexes in the presence of KOH.[4] Previously, Suzuki, Miyaura, and co-workers,[5] Percec and co-workers,[6] and Han and co-workers[7] proposed that the phosphate anion may coordinate to the metal center of the oxidative-addition product through a ligand-exchange step. Shi and co-workers reported the formation of borate from aryloxylate and boronic acid derivatives.[8] Moreover, our ongoing interest in phosphoric-carboxylic mixed anhydride reactivities[9] led us to propose a new borophosphate species (Scheme 2)[10] that may be involved in the transmetalation step.



$$\mathrm{ArOP(O)(OEt)_2} + \mathrm{(HO)_2B{\sim}Ar'} \xrightarrow[\substack{K_3PO_4 \\ \text{1,4-dioxane, heat}}]{[Ni(PCy_3)_2Cl_2]} \mathrm{Ar{-}Ar'}$$

Scheme 1. Nickel-catalyzed cross-coupling of aryl phosphates with arylboronic acids.



Scheme 2. Proposed active species (Ar = aryl).

Herein, we report a detailed theoretical and experimental study on the reaction mechanism of the nickel-catalyzed SMC reaction of aryl phosphates with arylboronic acids. In the density functional theory (DFT) calculations, the model catalyst $Ni(PCy_3)_2$, diethyl phenyl phosphate, and phenylboronic acid were used. Relative free energies are employed to analyze the reaction mechanism.

In general, three basic steps (oxidative addition, transmetalation, and reductive elimination) are included to study the mechanisms of the SMC reactions, as exemplified by a number of recent theoretical studies.[11] Two possible pathways for the oxidative addition step in our model reaction are considered in Figure 1 (paths A and B), based on the palladium- and nickel-catalyzed C–X (X = O, Cl, Br, I) activation reactions.[11b,12] Both processes start with a bis-ligated Ni^0 species, which is generated from the catalyst precursor $[Ni(PCy_3)_2Cl_2]$ in the presence of arylboronic acid and K_3PO_4. Path A involves the direct coordination of the bi-

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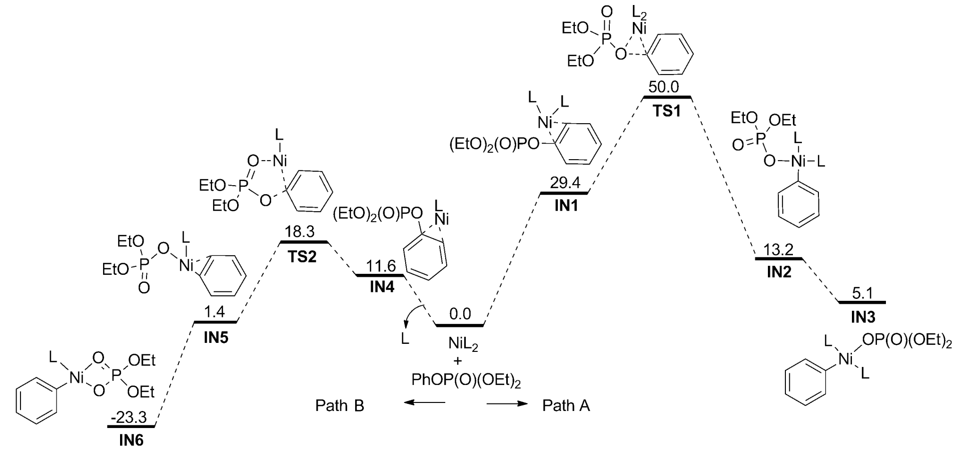


Figure 1. Gibbs energy profile for the oxidative addition step in the nickel-catalyzed cross-coupling of diethyl phenyl phosphate with phenylboronic acid; L = PCy_3 (in kcal mol^{-1}).

sphosphine NiL_2 complex to $PhOP(O)(OEt)_2$ to generate an unstable intermediate, **IN1** (29.4 kcal mol^{-1}). Subsequent oxidative addition from **IN1** proceeds through a three-membered transition state, **TS1**, thus leading to a four-coordinated *cis*-Ni^{II} complex, **IN2**, which can easily isomerize into the more-stable *trans*-Ni^{II} complex, **IN3**.[11d] Path B starts with a monophosphine η^2 complex, **IN4**, which is formed by the removal of one phosphine ligand from NiL_2, followed by a coordination to $PhOP(O)(OEt)_2$. Immediate **IN5** is formed through five-centered transition state **TS2**, which can isomerize into a four-coordinated Ni^{II}–monophosphine complex, **IN6**, which is more stable than **IN3** by 28.4 kcal mol^{-1}, thus suggesting that path B is kinetically and thermodynamically favorable for the oxidative addition step.

To investigate the role of the potassium phosphate in the transmetalation step, we first calculated the base-free pathway (Figure 2). Coordination of the phenylboronic acid to species **IN6** can generate two types of Ni^{II} intermediates, **IN7** and **IN7′**, which undergo six- (**TS3**) and four-membered transition states (**TS3′**) to form **IN8** and **IN8′**, respectively. The overall barriers for this transmetalation step were computed to be 51.6 (**TS3**) and 49.8 kcal mol^{-1} (**TS3′**). Therefore, the base-free pathway is not energetically feasible, in line with the experimental observations that this reaction cannot occur without the present of the base.

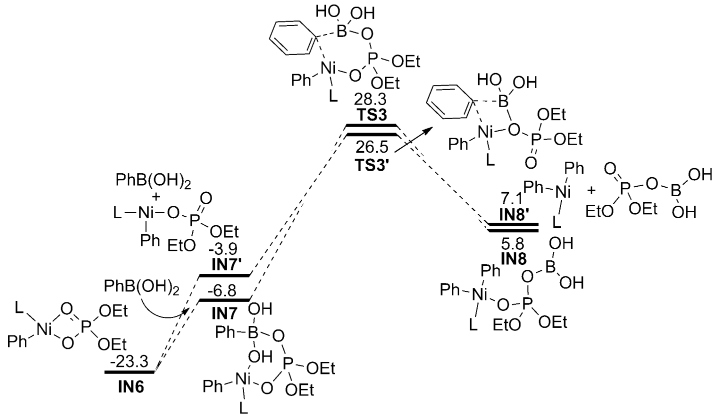
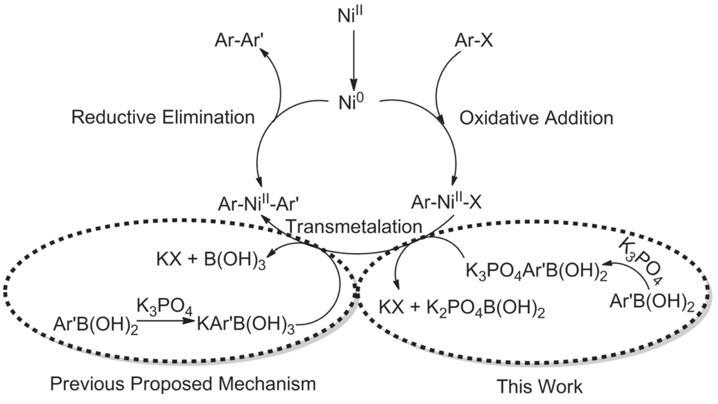


Figure 2. Gibbs energy profile for the base-free transmetalation step in the nickel-catalyzed cross-coupling of diethyl phenyl phosphate with phenylboronic acid; L = PCy_3 (in kcal mol^{-1}).

Next, we turned our attention to the base-assisted transmetalation step. In the previous calculations of Ni-catalyzed SMC reactions (Scheme 3), Liu and co-workers[11b] and Houk and co-workers[11e] proposed that the active species that participated in the transmetalation step were borate anions ($ArB(OH)_3^-$) that were formed in situ from arylboronic acid and K_3PO_4. However, the only experimental evidence for the involvement of the borate anions in the transmetalation step was their presence in the reaction mixture.[13] In 2011, Shi and co-workers reported a new Ni-catalyzed SMC reaction and successfully isolated a key intermediate borate species.[8] In addition, a clear change in yield was reported by using different bases in a variety of nickel-catalyzed SMC reactions. For most of these reactions, the optimal reaction conditions favored potassium phosphate as the base.[2] To the best of our knowledge, no solid evidence has been reported to address the effect of potassium phosphate. Herein, we propose a new transmetalation pathway that is mediated by a reactive anhydride species, borophosphate (Figure 3). This transmetalation reaction begins with the interaction of phosphate with phenylboronic acid, which generates an active species, borophosphate. This species coordinates with the Ni^{II} complex, **IN6**, to form a slightly stable intermediate, **IN9**. In species **IN9**, three potassium cations are coordinated to P-bonded oxygen atoms and the B–OH groups. The distances between K^+ and oxygen atoms range from 2.627–2.908 Å. The subsequent dissociation of $KOP(O)(OEt)_2$ leads to the formation



Scheme 3. Mechanism of the nickel-catalyzed Suzuki–Miyaura reaction.

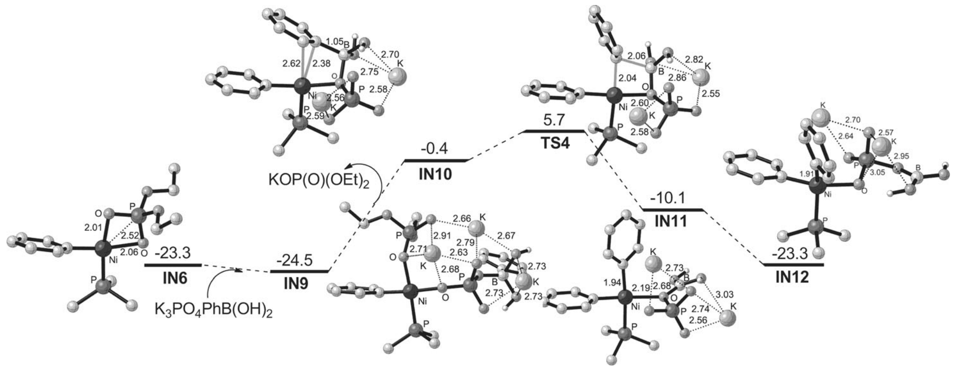


Figure 3. Gibbs energy profile for the base-mediated transmetalation step in the nickel-catalyzed cross-coupling of diethyl phenyl phosphate with phenylboronic acid (in kcal mol^{-1}).[14] PCy_3 was used as a ligand in the calculations. For clarity, the cyclohexyl groups on the ligand and the C–H hydrogen atoms are not shown.

of tetracoordinated Ni^{II} complex **IN10**, which is converted into the transmetalation product through a four-membered transition state, **TS4**. The overall barrier of this borophosphate-assisted transmetalation step is 30.2 kcal mol^{-1}, in line with the experimental observation that this reaction was carried out at 110 °C.[15] Notably, this barrier is much smaller than those for the base-free transmetalation reaction (Figure 2), which can mainly be attributed to the activation of the C–B bond by the borophosphate. For instance, the C–B bond length (1.645 Å) in **IN10** is much longer than those in **IN7** and **IN7′** (1.618 and 1.571 Å, respectively). Accordingly, the bond order of the C–B bond in **IN10** (0.73) is smaller than those in **IN7** and **IN7′** (0.81 and 0.88, respectively). Moreover, the C–B bond length (2.056 Å) in **TS4** is also shorter than those in **TS3** and **TS3′** (2.138 and 2.112 Å, respectively). Therefore, breaking the C–B bond in the borophosphate-assisted transmetalation step is much easier than that in the base-free process.

Finally, the reductive elimination step shown in Figure 4 was not energy-demanding. This process was completed through a monophosphine pathway to avoid steric interactions between the two bulky phosphine ligands. After removal of the $K_2PO_4B(OH)_2$ species, a tricoordinated Ni^{II} complex, **IN15**, was formed. The corresponding transition state, **TS6**, was only 5.0 kcal mol^{-1} higher in energy than complex **IN15**. The formation of the C–C bond completes the catalytic cycle by regenerating NiL_2.

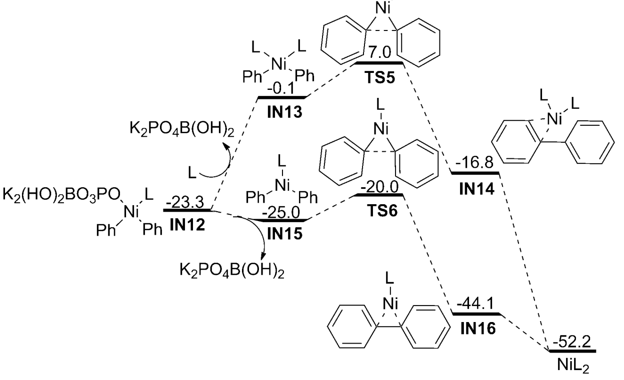


Figure 4. Gibbs energy profile for the reductive elimination step in the nickel-catalyzed cross-coupling of diethyl phenyl phosphate with phenylboronic acid; $L=PCy_3$ (in kcal mol^{-1}).

To test the reasonability of our model reactive species, we examined the interactions between the phosphate and phenylboronic acid by ^{31}P NMR spectroscopy. A mixture of potassium phosphate (0.15 mmol) and phenylboronic acid (0.15 mmol) in water was followed by ^{31}P NMR spectroscopy (Figure 5). Initially, there was only one signal in the spectrum, which was assigned to K_3PO_4 ($\delta_a=5.2$ ppm). Then, a new phosphorus-containing species was formed over time ($\delta_b=3.1$ ppm). Although this species was not stable enough to be characterized by HRMS and could not be crystallized, thus leading to uncertainty over its structure, a very similar species, $B(OH)_2CO_3^-$, was reported by McElligott and Byrne.[16]

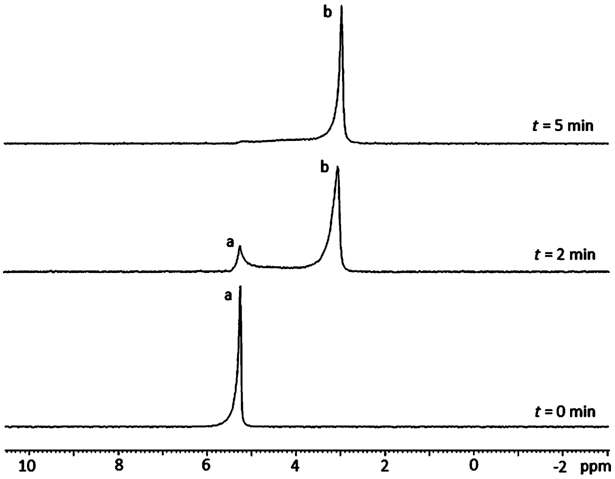


Figure 5. ^{31}P NMR study of the interaction between phosphate and phenylboronic acid.

In summary, we have studied the mechanism of the nickel-catalyzed cross-coupling of aryl phosphates with arylboronic acids both experimentally and computationally. Our results reveal that, in the oxidative addition and reductive elimination steps, the monophosphine-ligand pathway is preferred to the bis-ligated one. More importantly, potassium phosphate was found not to act as a spectator base but rather was involved in the transmetalation step. Thus, our findings provide key insight into the mechanism of the nickel-catalyzed Suzuki–Miyaura reactions and open a new avenue to the design of efficient catalysts.

Acknowledgements

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Keywords: cross-coupling · density functional calculations · nickel · reaction mechanisms · Suzuki–Miyaura reaction

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[15] The barrier was evaluated according to the Eyring equation, that is, $k=(k_{\mathrm{B}}T/h)\exp(-\Delta G^{\neq}/RT)$, where k is the rate constant, k_{B} is the Boltzmann constant, T is the temperature, $\Delta G^{\neq}$ is the free energy of activation, R is the gas constant, and h is Planck's constant. Assuming that the half-life of this reaction is 24 h and that the concentration of each reactant is 1 mol L^{-1}, the second-order rate constant k is equal to 1.2×10^{-5} L mol^{-1} s, we obtained that at 110 °C, $\Delta G^{\neq}$ is 31.4 kcal mol^{-1}.

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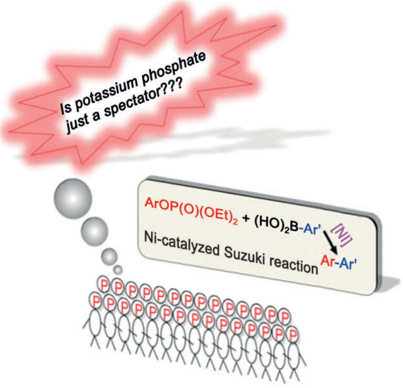
Spectator or actor? Density functional theory calculations were performed to examine the role of the base in the nickel-catalyzed cross-coupling of aryl phosphates with arylboronic acids. Potassium phosphate was found to not act as a spectator base but was involved in the transmetalation step, as shown by a lower barrier than that of a base-free process, owing to the activation of the carbon–boron bond by the base. Further experimental observations support the theoretical findings.



Reaction Mechanisms

Liu Liu, Shuangyan Zhang, Hu Chen, Ye Lv, Jun Zhu, Yufen Zhao** ▮▮▮▮–▮▮▮▮

Mechanistic Insight into the Nickel-Catalyzed Cross-Coupling of Aryl Phosphates with Arylboronic Acids: Potassium Phosphate is Not a Spectator Base but is Involved in the Transmetalation Step in the Suzuki–Miyaura Reaction