

Theoretical Investigations of Palladium-Catalyzed Cross-Coupling of Alkenyl Carboxylates

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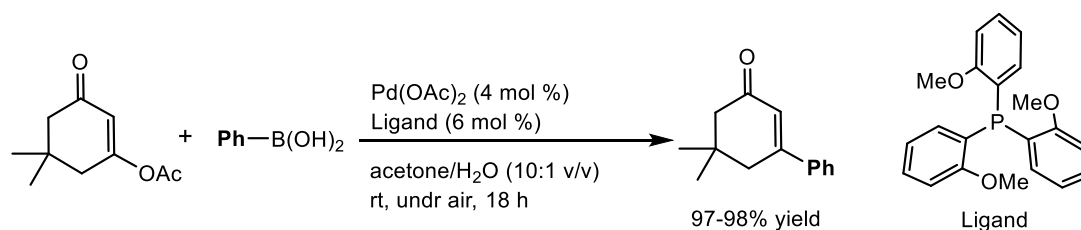
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Transition-metal-catalyzed coupling reactions of alkenyl carboxylate with boronic acids are rare, and those that have been reported are often limited by a narrow range of substrates and high-temperature requirements. The palladium-catalyzed cross-coupling reaction of alkenyl carboxylate¹ reported by Leitch, *et al.* proceeds at room temperature over a wide range of substrates without bases. Pd(OAc)₂ and Pd(PCy₃)₂ have been used as catalysts, and it has been confirmed that when Pd(PCy₃)₂ is used, intermediates with oxidative addition of the catalyst are obtained. It has been proposed that the two reactions proceed by different mechanisms. However, the detailed reaction mechanisms of these reactions have not been clarified. We investigated the detailed reaction mechanisms using DFT calculations.

Two catalytic cycles (Pd(0/II) and Pd(II) cycles) of Pd(PCy₃)₂ and Pd(OAc)₂ were investigated: the Pd(0/II) cycle consists of oxidative addition, transmetalation, and reductive elimination. The Pd(0/II) cycle consists of three steps: oxidative addition, metal exchange, and reductive elimination. The activation energy of the oxidative addition step is 109.6 kJ/mol, suggesting that the cycle does not proceed at room temperature. It was also suggested that the transmetalation step is energetically more favorable for bis-PCy₃ coordinated systems rather than mono-PCy₃ coordinated pathway.

The Pd(II) cycle consists of four steps: transmetalation, syn-carbopalladation, epimerization via a 1,3-palladotropic shift, and β-OAc elimination. The energy of the transition state in the syn-carbopalladation step is the highest, suggesting it is the rate-determining step.

Comparison of these catalytic cycles shows that the rate-determining step has lower energy in the Pd(II) cycle than in the Pd(0/II) cycle, which is consistent with the experimental results showing that the process proceeds at room temperature with the Pd(II) catalyst.



1) J. Becica, O. R. J. Health, C. H. M. Zheng, D. C. Leitch, *Angew. Chem. Int. Ed.* **2020**, 59, 1-6.