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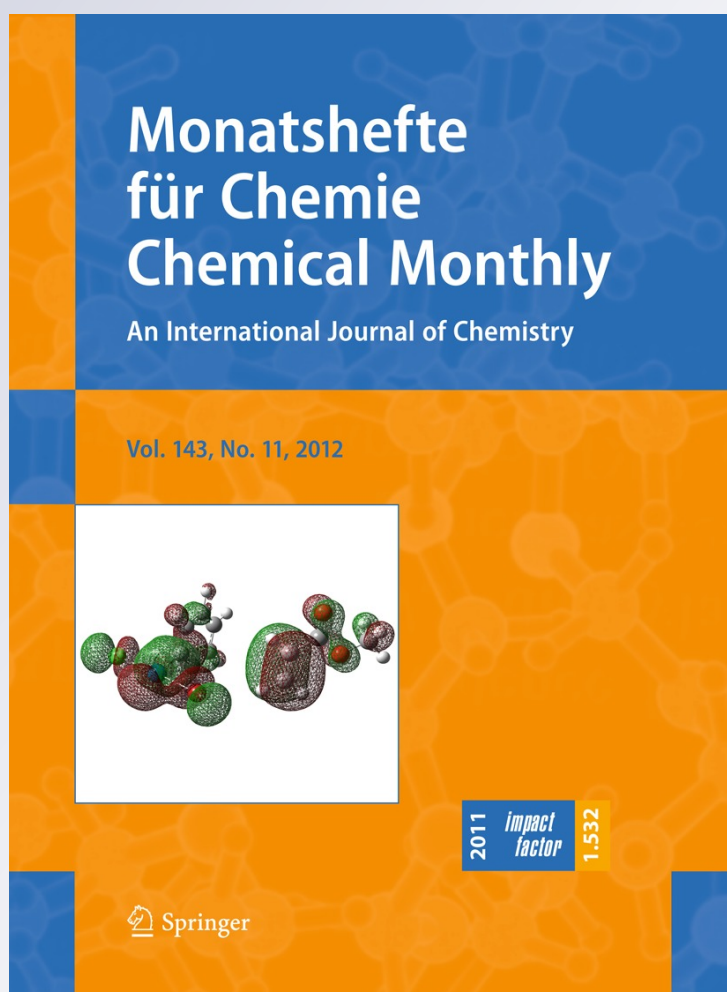
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Mechanistic insight into the formation of cinnamates in phosphine-free Heck reactions

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Abstract A mechanistic study of the formation of cinnamates in phosphine-free Heck reactions was performed. Pathways for migratory insertion, β -hydride elimination, and catalyst recovery were elucidated using density functional theory (DFT) methods. It was shown that catalyst recovery is the rate-determining step of the overall Heck catalytic cycle.

Keywords Reaction mechanisms · Migratory insertion · β -Hydride elimination · Catalyst recovery · Density functional theory

Introduction

Cinnamates are widely distributed in the plant kingdom. They are synthesized by plants and are components of essential oils. Recent studies have demonstrated that such essential oils exhibit different kinds of biological activity, such as antioxidative, antibacterial, antifungal, antithrombotic, and anti-inflammatory activity [1–5]. Synthetic methyl cinnamate is a substance widely used as a flavor or fragrance ingredient.

One of the most powerful modern synthetic methods for the preparation of cinnamates is the Pd-catalyzed Heck reaction. This reaction is one of the most versatile and

feasible tools for C–C bond formation [6–16]. A lot of work has been devoted to the elucidation of the catalytic pathways where phosphines have been used as ligands [13–22]. Phosphine-free Pd complexes have been introduced as a less complicated and environmentally more desirable alternative to the original Pd-phosphine catalysts [8–12, 23–28].

The mechanism of the Heck reaction attracts the attention of both experimental and theoretical chemists [25–39]. It has been established that the Heck reaction proceeds through a preactivation process where a catalytically active Pd(0) complex is formed [25, 27, 28], oxidative addition of aryl halide to Pd(0) species, which is considered a key step in the mechanism of Pd-mediated cross-coupling reactions [14–18, 21, 22, 27, 40], migratory insertion, and β -hydride transfer/reductive elimination [41–48].

In our previous studies, we reported the efficiency of the *trans*-dichlorobis(diethanolamine-*N*)palladium(II) complex (*trans*-[PdCl₂(DEA)₂]) in the Heck coupling reaction of different aryl halides with acrylates in the presence of different bases [25, 27] and ionic liquids [23], and proposed the mechanisms of catalyst preactivation and oxidative addition. In a recent paper we reported the results on the migratory insertion, β -hydride elimination, and catalyst recovery for the model reaction of methyl methacrylate with some aryl halides [49]. These steps of the Heck reaction have not been investigated with similar phosphine-free Pd catalysts and substrates. This fact prompted us to examine possible mechanistic pathways of these reaction steps for another model reaction.

Results and discussion

The subject of the present investigation is the mechanism of migratory insertion, β -hydride elimination, and catalyst

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