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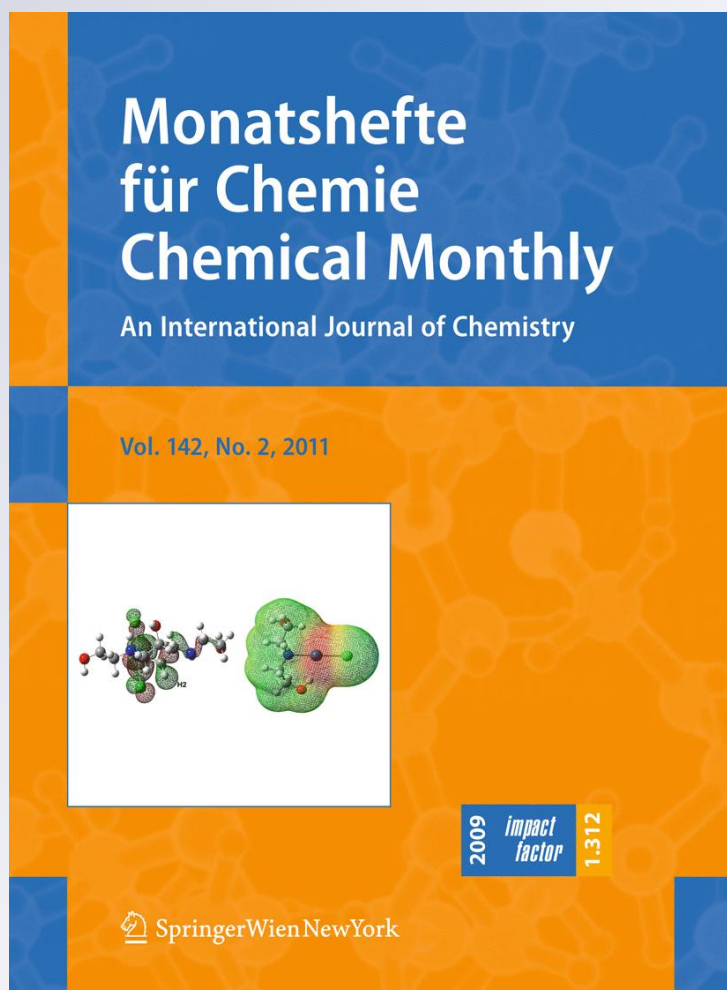
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# A new aspect of Heck catalyst formation

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**Abstract** The mechanism of the formation of the active Pd(0) complex from *trans*-dichlorobis(diethanolamine-*N*)palladium(II) complex in the presence of strong base was investigated by using density functional theory (M06 method). Our investigation shows that in the basic environment *trans*-dichlorobis(diethanolamine-*N*)palladium(II) complex undergoes abstraction of the alcoholic proton, and coordination of alkoxide oxygen to palladium. The intermediate complex, in which hydrogen is coordinated to Pd, undergoes reductive elimination of HCl, yielding the catalytically active low ligated Pd(0) complex.

**Keywords** Heck reaction · Reaction mechanism · Preactivation process · Catalytically active Pd(0) complex · Density functional theory

## Introduction

The palladium-catalyzed arylation of olefins, known as the Heck reaction, is one of the most important methods for carbon–carbon bond formation in organic synthesis [1–4]. Because of its increasingly expanding use and importance, the Heck reaction attracts attention of both experimental [5–9] and theoretical chemists [10–22]. Owing to the significant synthetic versatility of palladium-catalyzed cross-coupling reactions, the Nobel Prize for chemistry for 2010

was awarded to Richard F. Heck, Ei-ichi Negishi, and Akira Suzuki. On the basis of their methodologies, numerous fine chemicals and commercially available aromatic substrates were produced [23].

In spite of the fact that the Heck reaction has significant relevance in industry during the last two decades, the complex mechanism of this reaction has not been elucidated. Confusion arises, especially, when Pd(II) complexes are used as precatalysts, generating in situ Pd(0) active species [24]. Much effort has been devoted to the elucidation of the Heck reaction mechanism [10–12], including oxidative addition [15–21] and reductive elimination [22, 25]. On the other hand, very little is known about the mechanism of formation and molecular structure of Pd(0) complexes [13, 14] generally accepted as the catalytically active forms.

In our previous studies, the *trans*-dichlorobis(diethanolamine-*N*)palladium(II) complex (**1**), whose structure was reported earlier [13, 14, 26], has been used as a catalyst precursor in phosphine-free Heck reactions. The reactions between different olefins and aryl halides catalyzed with **1** have been studied in the presence of a weak base (diethanolamine), strong base (NaOEt) [13, 14], and ionic liquids (diethanolammonium acetate and diethanolammonium chloride) [27], where Pd(II) precatalyst was obtained in situ. Now we wish to report a new aspect of the preactivation reaction of the Heck catalyst precursor.

## Results and discussion

Here we present the results of our investigation of the mechanism of formation of the Pd(0) catalyst in the presence of a strong base in acetonitrile as reaction medium. Acetonitrile was selected as solvent because it was used in

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