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Mechanistic pathways for oxidative addition of aryl iodides to the low-ligated diethanolamine palladium(0) complex in phosphine-free Heck reactions

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ABSTRACT

A set of reactions of different activated olefins and aryl iodides with the *trans*-dichlorobis(diethanolamine-*N*)palladium(II) complex (*trans*-[PdCl₂(DEA)₂]) as a precatalyst was performed, in the presence of diethanolamine (DEA) as a weak base, and NaOEt as a strong base. It was established that the presence of NaOEt slightly lowered the yields, but significantly accelerated the reactions. This experimental finding is in agreement with our computational investigation that shows that significantly higher activation barrier is required for the preactivation reaction in the presence of a weak base than in the presence of a strong base. The reaction between the catalytically active DEA–Pd(0)–Cl complex, formed in the preactivation reaction, and iodobenzene was investigated using density functional theory. Two mechanisms for the oxidative addition of the activated complex were found. The first mechanism is based on a nucleophilic attack of Pd on I of iodobenzene, and yields an intermediate tetracoordinated Pd complex (aI2). The second mechanism begins with a nucleophilic attack of Pd on the benzene ring, and yields a tricoordinated intermediate complex (bI4). It was concluded, on the basis of structural and energetical properties of aI2 and bI4, that the second mechanism is significantly more favorable. It was shown that the oxidative addition requires noticeable lower activation energy than that required for the preactivation process. Thus, our investigations indicate that oxidative addition is not the rate determining step for the Heck reactions investigated in this work, but preactivation step.

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1. Introduction

Organic reactions catalyzed with transition metals usually occur in series of steps. In each step, there are reactive intermediates as products, of which at least one contains σ carbon–metal bond. A class of such reactions includes palladium-catalyzed cross-coupling reactions of arylation of olefins, known as the Heck reactions [1–7]. These reactions have major impact on organic chemistry due to their significant synthetic versatility [8–10].

In our previous studies [11,12] we have elaborated the preactivation steps of a phosphine-free Heck reaction, where as a precatalyst we used *trans*-dichlorobis(diethanolamine-*N*)palladium(II) complex (*trans*-[PdCl₂(DEA)₂]). Synthesis and structural characterization of this complex has been reported in Ref. [13]. It was established that DEA–Pd(0)–Cl was obtained in the preactivation process of the investigated reaction (step **a**, Scheme 1).

The next step in the Heck catalytic cycle is oxidative addition of aryl halide to Pd(0) species. This step has been the subject of much investigation [14–21], and is considered to be the rate determining

process. Oxidative addition usually involves coordinatively unsaturated Pd(0) complexes [15–17,21–23]. A lot of work has been devoted to the elucidation of the catalytic pathways where phosphines are used as ligands [14–18,22–24], whereas the results regarding non-phosphine ligands are scarce [19,20,25–31]. Hence, the aim of this experimental and DFT study is to investigate possible ways of oxidative addition of aryl iodides to the preactivated Pd(0) complex (DEA–Pd(0)–Cl).

2. Results and discussion

Our recent experimental works confirmed that the *trans*-dichlorobis(diethanolamine-*N*)palladium(II) complex can be useful precatalyst in phosphine-free Heck reactions [11]. The mechanism of the initial preactivation process, solvent effects, and acceleration of the reaction induced with a strong base (NaOEt), were examined using density functional theory (DFT) [12]. It was deduced that the DEA–Pd(0)–Cl complex is obtained in step **a** of the reaction, and that it is catalytically active form (Scheme 1).

Now we investigate possible mechanistic pathways for oxidative addition, (step **b** in Scheme 1), of aryl iodides to the low-ligated diethanolamine palladium(0) complex. It is believed that oxidative addition is crucial and rate determining step of the Heck

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