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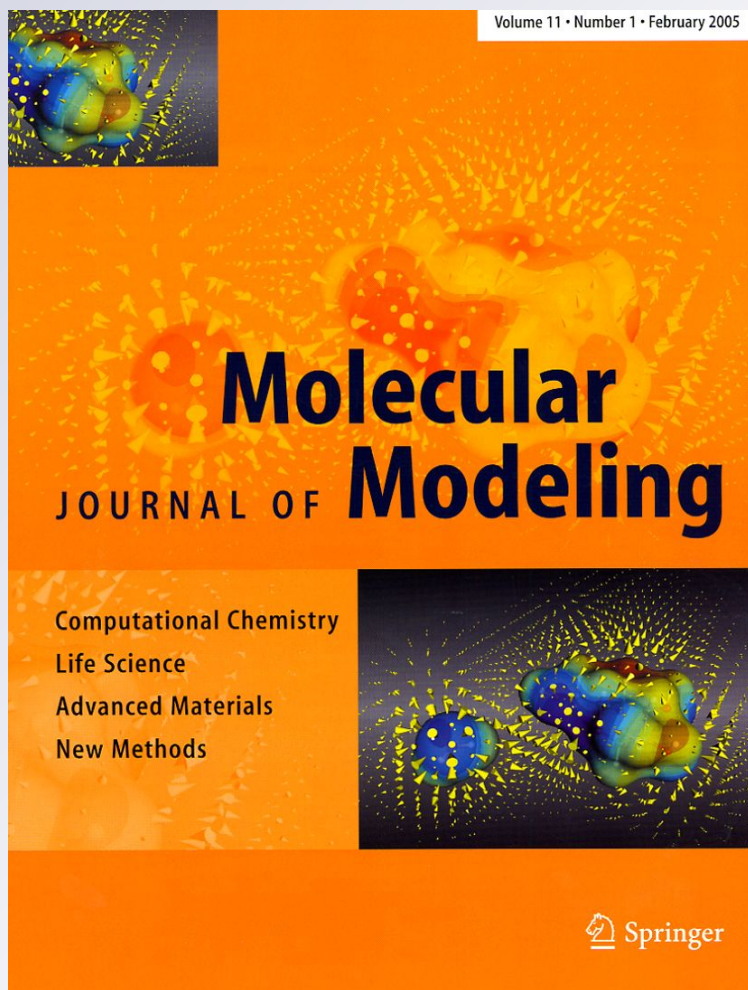
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Triethanolammonium acetate as a multifunctional ionic liquid in the palladium-catalyzed green Heck reaction

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Abstract An efficient green Heck reaction protocol was performed using a triethanolammonium acetate ionic liquid–palladium(II) catalytic system. The ionic liquid used acts as a reaction medium, base, precatalyst-precursor, and mobile support for the active Pd species. Our experimental investigation indicates that performing the Heck reaction in ionic liquid is superior to the same procedure carried out in triethanolamine. The mechanism of the reaction of triethanolammonium acetate with PdCl₂ was examined using density functional theory (M06 method). It was found that two Pd(II) complexes are formed, one of which acts further as a precatalyst yielding catalytically active Pd(0) complex. The calculated activation energies are in agreement with our experimental findings.

Keywords Triethanolamine ionic liquid · Green Heck reaction · Reaction mechanism · Pd(II) precatalyst · Pd(0) catalytically active complex

Introduction

The palladium-catalyzed arylation of olefins, known as the Heck reaction, is one of the most important methods of carbon–carbon bond formation in organic synthesis [1–4]. Due to its synthetic versatility, the Heck reaction attracts the

attention of both experimental [5–9] and theoretical chemists [10–22]. Much effort has been devoted to elucidation of the Heck reaction mechanism [10–12], including catalyst preactivation [13, 14], oxidative addition [15–21], and reductive elimination [22, 23].

In the last decade, phosphine-free Pd complexes have been introduced as a less complicated and environmentally more desirable alternative to the original Pd-phosphine catalysts [1]. In addition, the application of ionic liquids has been put forward as a very useful substitute for hazardous and volatile polluting organic solvents [24–27]. One of the predominant applications of ionic liquids focuses on homogeneous catalysis [24, 28]. Nowadays, multifunctional ionic liquids that can serve as good coordinating ligands, green solvents, as well as recyclable and mobile supports for palladium catalyst systems, are used. Functional groups that can complex palladium, such as amine, amide, nitrile, ether, alcohol, urea or thiourea [29, 30] have been introduced into the cationic and/or anionic moiety of ionic liquids.

Here, we report the use of triethanolammonium acetate [TEA][HOAc] as a multifunctional ionic liquid in a green Heck reaction. The investigated ionic liquid acts as a green solvent, base, precatalyst-precursor, and mobile support for the active Pd species. Our work focused on testing the efficiency of the obtained ionic liquid–palladium catalytic system in the Heck reaction, and on a density functional theory (DFT) investigation of the possible mechanism of in situ formation of the Pd(II) precatalyst. Since very little is known about the mechanism of formation and molecular structure of Pd(0) complexes [13, 14], which are generally accepted as the catalytically active forms, our additional goal was to elucidate the mechanism of reduction of the Pd(II) precatalyst to the catalytically active Pd(0) form.

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