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## Diethanolamine and N,N-diethylethanolamine ionic liquids as precatalyst-precursors and reaction media in green Heck reaction protocol

Zorica D. Petrović\*, Dušica Simijonović, Vladimir P. Petrović, Svetlana Marković

Faculty of Science, University of Kragujevac, P.O. Box 60, 34000 Kragujevac, Serbia

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## ABSTRACT

It was found that Heck reaction with  $\text{PdCl}_2$  in diethanolamine and N,N-diethylethanolamine ionic liquids (ILs) is more efficient than analogous reactions performed in classical organic solvents. The used ILs facilitate solubility of the Pd(II) precatalysts, increase catalyst stability during the reaction, and function as reaction media, bases, precatalyst-precursors, good coordinating ligands, and mobile support for active Pd species. Thus, Heck reaction occurs without additional solvents, ligands and bases, that makes experimental procedure much simpler. Our DFT investigation provides mechanistic insight into the formation of the  $\text{trans-[PdCl}_2(\text{DEA})_2]$  complex that acts as a precatalyst.

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## 1. Introduction

The palladium-catalyzed arylation of olefines, known as Heck reaction, is one of the most important methods for carbon–carbon bond formation in organic synthesis [1–6]. 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 applications of ionic liquids as very useful substitutes for hazardous and volatile polluting organic solvents have been put forward [7–17]. Unlike classical salts, whose melting points are not below 800 °C, most of ionic liquids (ILs), which also contain positively and negatively charged ions, are liquids at room temperature. Room temperature ionic liquid (RTIL), molten salt, liquid organic salt, and fused salt—all these terms have been used to describe new class of magical chemicals accepted from chemical industry and academia [18]. As solvents, ILs show several advantages which make them more attractive and ecologically acceptable [19–26]: (1) They are good solvents for a wide range of organic, inorganic and organometallic compounds, (2) They are polar, (3) ILs are immiscible with a number of organic solvents and provide a polar nonaqueous alternative for biphasic catalytic systems, implying that the molecular catalyst is soluble in only one phase, whereas the substrates/products remain in the other, (4) Most of ILs are liquid up to 200 °C, (5) ILs are thermally stable (are not explosive and flammable), and

do not evaporate since they have very low vapour pressures. All these features significantly distinguish ILs from classical volatile and toxic organic solvents, and therefore, ILs are named green solvents.

Ionic liquid as reaction medium for the palladium-catalyzed Heck reaction was for the first-time described in 1996 [27]. But, the process of preparing effective non-phosphine ligands and recyclable catalysts from ordinary ionic liquids was very complex, because of their weak coordinating abilities [28–34]. Recently, some efforts have been made in order to prepare low cost multi-functional ionic liquids that could serve as green solvents, coordinating ligands, as well as recyclable and mobile support for palladium catalyst systems. For this reasons, researchers started to use ionic liquids with additional functional groups in cationic and/or anionic part of ionic liquid molecules. Functional groups that can complex palladium, such as amine, amide, nitrile, ether, alcohol, urea or thiourea [29,35–38] have been introduced into the ILs. Such ionic liquids have been found to demonstrate high solvation capabilities, and low viscosity. These properties made them useful in a broader range of applications.

Here, we wish to report the use of diethanolamine (DEA) and N,N-diethylethanolamine (DEAE) ionic liquids, which act as green solvents, precatalyst-precursors, and mobile support for active Pd species in phosphine-free Heck reaction protocol. In addition, the optimization of the ILs structures, as well as investigation of a possible mechanism for in situ formation of Pd precatalyst, was performed using density functional theory.

\* Corresponding author. Tel.: +381 34 336223; fax: +381 34 335040.

E-mail address: [zorica@kg.ac.rs](mailto:zorica@kg.ac.rs) (Z.D. Petrović).









