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Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Stereoselective homogeneous catalytic arylation of methyl methacrylate: Experimental and computational study

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ARTICLE INFO

Article history:

Received 26 October 2011

Received in revised form

20 December 2011

Accepted 9 January 2012

Available online 16 January 2012

Keywords:

Homogeneous catalysis

Migratory insertion

 β -Hydride elimination

Diethanolamine palladium complex

Density functional theory

ABSTRACT

Catalytic systems $\text{trans-[PdCl}_2(\text{DEA})_2]/\text{DEA}$ and $\text{trans-[PdCl}_2(\text{DEA})_2]/[\text{DEA}][\text{HAc}]$, used in the model reaction of methyl methacrylate with iodobenzene, 4-iodoanisole, and bromobenzene, provide homogeneous catalysis, good regioselectivity and excellent stereoselectivity. The major product of the regioselective reaction is internal olefin. In all examined cases the only stereoisomer of the internal olefin methyl 3-phenyl-2-methylpropenoate is the E-isomer, whereas the only stereoisomer of the double arylated reaction product methyl 2-benzyl-3-phenylpropenoate is the Z-isomer. A DFT study, which investigates mechanistic aspects of migratory insertion, β -hydride elimination and reductive elimination of this phosphine-free Heck reaction, is in agreement with our experimental findings.

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1. Introduction

Among palladium-catalyzed reactions, the arylation and vinylation of alkenes, known as the Heck reaction, is one of the most important carbon–carbon bond forming processes [1–7]. This reaction has major impact on organic chemistry due to its significant synthetic versatility and possibility for countless complex organic molecules to be prepared [8–10]. Over the last two decades an impressive number of applications have been developed at the laboratory and industry. The Heck reaction becomes more interesting when the used alkene is disubstituted, what allows different regio- and stereoselectivity. To achieve synthesis of one regio- or stereoisomer of a trisubstituted alkene with high yield is still a challenge in modern synthetic organic chemistry. One of the most important and difficult targets is the control of the configuration of the double bond, the E- and Z-selectivity.

A lot of work has been devoted to the elucidation of the Heck reaction pathways where phosphines are used as ligands [11–18], whereas the results regarding non-phosphine ligands are scarce [19–22]. Mechanistically, the Heck reaction is a multistep organic reaction, whereby at least one intermediate contains σ carbon–metal bond. The Heck reaction mechanism, which can be

anionic, cationic, or neutral, attracts attention of both experimental and theoretical chemists [23–37].

The preactivation reaction of a phosphine-free Heck reaction, where *trans*-dichlorobis(diethanolamine-*N*)palladium(II) complex ($\text{trans-[PdCl}_2(\text{DEA})_2]$) was used as a precatalyst [30–32], has recently been elaborated. It was established that the catalytically active DEA-Pd(0)-Cl complex was obtained in the preactivation process [30–32]. The next step in the Heck catalytic cycle, oxidative addition of aryl halide to Pd(0) species, is considered a key step in the mechanism of Pd-mediated cross-coupling reactions, and usually involves coordinatively unsaturated Pd(0) complexes [11–16,34]. The reaction further proceeds through the migratory insertion and β -hydride transfer/reductive elimination steps [38–45].

The aim of this experimental and DFT study is to investigate possible ways of migratory insertion, β -hydride and reductive elimination of phosphine-free Heck reaction, where a disubstituted alkene methyl methacrylate is used as a substrate. In the Heck reaction of aryl halides with methyl methacrylate, biologically active and useful trisubstituted olefins with broad applications in pharmaceutical industry (for example α -methylcinnamates) can be obtained. These compounds show interesting physico-chemical properties, too. In order to provide sustainable green homogeneous catalysis, beside DEA as solvent, the ionic liquid (IL) diethanolammonium acetate ([DEA][HAc]) was also used as reaction medium.

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