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Oxidative coupling of benzoic acids with alkynes: Catalyst design and selectivity

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Dedicated to 85th anniversary of Prof. Irina P. Beletskaya in recognition of her outstanding contribution to the development of the metal-complex catalysis.

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ABSTRACT

The review covers the mechanism insights and recent achievements in catalyst design for oxidative coupling of benzoic acids and alkynes. This reaction is a straightforward effective approach to synthesis of isocoumarins or naphthalenes. The influence of catalyst nature and reaction conditions on the selectivity is also discussed. This contribution aims to focus attention of organic chemists on the possibility to use a wide range of catalysts, without being limited by only conventional complexes.

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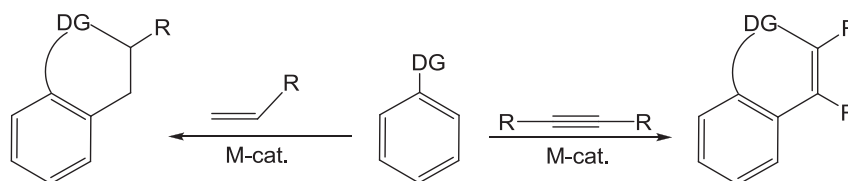
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1. Introduction

The search for efficient and economic ways to construct the C–C, C–O and C–N bonds is one of the important tasks of modern

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Scheme 1. Metal-catalyzed coupling of benzene derivatives with alkenes or alkynes.

chemistry. The metal-complex catalysis has proved to be the most efficient approach to solve this problem. In particular, it leads to decrease of time and recourses for synthesis as compared with conventional methods of organic chemistry. The palladium-catalyzed cross-coupling reactions (e.g., Heck, Suzuki and Sonogashira reactions) are the most known processes for formation of the C–C bond, which was evidenced by the Nobel Prize award in 2010 [1]. In order to simplify this strategy, Beletskaya developed the “ligandless” modification using palladium nanoparticles [2]. Nevertheless, these reactions still require the preliminary formation of the C–X bonds (where X is halogen) and lead to other products (like HX, salts, etc.). In contrast, the metal-catalyzed direct C–H activation is rather atom- and step-economic strategy [3].

Among transformations proceeding via C–H activation, annulation reactions of benzene derivatives with alkenes or alkynes are particularly interesting, because they produce biologically and photochemically active heterocycles, e.g. isocoumarins, indoles, naphthopyrans, dihydroisoquinolinones [4]. This approach is based on the chelation-assistance of an appropriate directing group (e.g., C(O)OH, C(O)NR₂, OH, pyrazole) that provides selectivity for C–H activation in *ortho* position (Scheme 1). Murai was a pioneer in development of this strategy [5]. In 1993, he showed that the Ru(0) complexes effectively catalyze coupling of aromatic ketones with alkenes involving regioselective C–H activation at the *ortho* position via chelation-assistance of carbonyl group. Since this work, the coupling of various benzene derivatives with alkenes and alkynes has been described.

Besides ruthenium complexes the classical palladium catalysts (e.g., Pd(OAc)₂) have also proved to be effective for the coupling reactions [6]. However, the Pd(II)/Pd(0) processes are limited by substrate scope (alkynes are almost inactive) and high catalyst loading (more than 5 mol%). Moreover, the palladium catalysts can undergo decomposition into inactive bulk metal [7]. Larock found that alkynes can be involved into palladium-catalyzed coupling reaction using only appropriate halogen- or triflate-substituted

benzene derivatives without direct C–H activation (Scheme 2) [8]. Various substituted isocoumarins were synthesized by this way. Another well-known palladium-catalyzed reaction giving isocoumarins, namely cyclization of *tert*-butyl-2-alkynylbenzoates with olefins, is also not a C–H activation process [9].

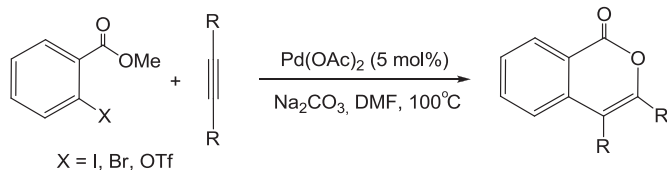
In contrast, the catalyst systems based on the Rh(III)/Rh(I) processes have the advantage of low catalyst loading, with reactions often being performed under mild conditions allowing broad functional group tolerance. In 2007, Satoh and Miura developed the direct oxidative coupling of benzoic acids with alkynes catalyzed by [Cp*₂RhCl₂] [10]. This reaction selectively produces ether isocoumarins (**1**) or naphthalenes (**2**) depending from reaction conditions and catalyst structure (Scheme 3). Since this key report appeared the rhodium-catalyzed oxidative couplings of various aromatic substrates with alkynes and alkenes have been extensively investigated. In particular, ketones [11], amides [12], imines [13], phenols [14], phenylpyridines [15] were successfully introduced in this reaction. We do not wish to cover here all of these organic transformations which are already well summarized in several excellent reviews [4]. Herein we report the recent advances in catalyst design, and analyze the influence of catalyst nature and reaction conditions on the selectivity of oxidative coupling of benzoic acids with alkynes. This reaction has a special importance in the synthesis of isocoumarins, which are structural motifs of compounds with important biological and fluorescent properties [16].

2. Oxidative coupling of benzoic acids with alkynes

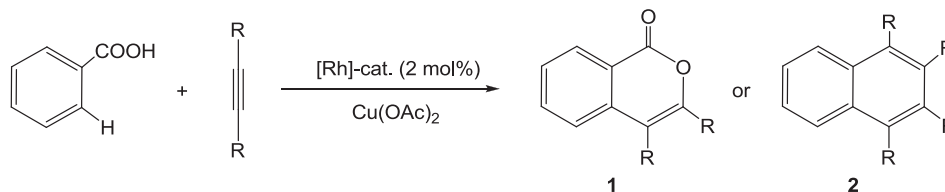
2.1. Mechanism

Satoh and Miura proposed the possible mechanism of two pathways of oxidative coupling of benzoic acid with alkynes (Scheme 4) [10b]. In both cases the reaction starts from the formation of the Rh(III) benzoate **A** as a result of coordination of catalyst to carboxylic group. Subsequent C–H activation of *ortho* proton gives five-membered rhodacycle intermediate **B**. Then alkyne insertion leads to seven-membered rhodacycle **C**. For the first pathway intermediate **C** undergoes reductive elimination of rhodium atom to produce isocoumarins **1**. In contrast, the formation of naphthalenes **2** (the second pathway) includes the decarboxylation of **C** with following insertion of second alkyne molecule into intermediate **D** and reductive elimination of rhodium.

In both cases the resulting Rh(I) species are oxidized by



Scheme 2. Pd-catalyzed coupling of halogen- or triflate-substituted esters with alkynes.



Scheme 3. Rh-catalyzed coupling of benzoic acid with alkynes.

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