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## Digest Paper

# Metal-catalyzed carbonylation of alkynes: key aspects and recent development

Samuel Quintero-Duque<sup>a</sup>, Katrin Marie Dyballa<sup>b</sup>, Ivana Fleischer<sup>a,\*</sup><sup>a</sup> Institute of Organic Chemistry, University of Regensburg, Universitätsstr. 31, 93040 Regensburg, Germany<sup>b</sup> Evonik Industries AG, Paul-Baumann-Str. 1, 45772 Marl, Germany

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## ABSTRACT

Carbonyl compounds represent an important class of synthetic intermediates in organic chemistry with growing industrial significance. Among the plethora of methods available for their synthesis, metal-catalyzed carbonylations constitute one of the most prominent ones, due to their efficiency, atom-economy, and often excellent selectivity. Carbonylations of alkynes give access to different types of compounds, such as unsaturated carboxylic acid derivatives or various heterocycles. Many of these products are bulk chemicals, biologically active compounds, or intermediates in the total synthesis. In recent years, considerable progress was made in this field, especially with commercial catalysts based on palladium, rhodium, and cobalt.

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\* Corresponding author. Tel.: +49 941 943 4628; fax: +49 941 943 4121.

E-mail address: [ivana.fleischer@ur.de](mailto:ivana.fleischer@ur.de) (I. Fleischer).

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## Introduction

Carbonylation reactions are based on the incorporation of a C=O moiety into substrates such as alkenes, alcohols, alkynes, alkyl halides, amines, and nitro compounds.<sup>1,2</sup> Catalytic carbonylations of unsaturated compounds have been known since the pioneering work of Walter Reppe and his team at BASF, Germany, during the 1930s and 1940s, who developed a number of carbonylation reactions catalyzed or promoted by metal carbonyl complexes.<sup>3–6</sup> They discovered the carbonylation of alkynes in the presence of protic nucleophiles, for example, the reaction of acetylene, carbon monoxide, and water to form acrylic acid, by using Ni(CO)<sub>4</sub> as a catalyst.<sup>7</sup>

Reppe's discoveries were applied for the commercial scale production of acrylic acids and esters. The later extension of this methodology to higher alkynes with the help of different transition metals led to the production of important monomers and synthetic building blocks, such as methyl methacrylate (MMA) and acrylamides. A major goal continues to be the development of chemo- and regioselective catalysts for carbonylation of higher alkynes in the presence of alcohols, amines or thiols for the synthesis of fine chemicals, pharmaceuticals, and their intermediates (Fig. 1). Intramolecular versions of these transformations and other cyclocarbonylations provide access to unsaturated carbonylated heterocycles.<sup>8,9</sup> Under oxidative conditions, various products of mono-, di-, and tricarboxylation can be obtained selectively. In addition, employment of synthesis gas (CO/H<sub>2</sub>) leads to the production of unsaturated aldehydes via hydroformylation.

Herein, we would like to summarize the most important developments in the carbonylation of alkynes, as well as selected recent catalytic accomplishments based on the use of transition metal

complexes. The review is structured according to the employed transition metal.

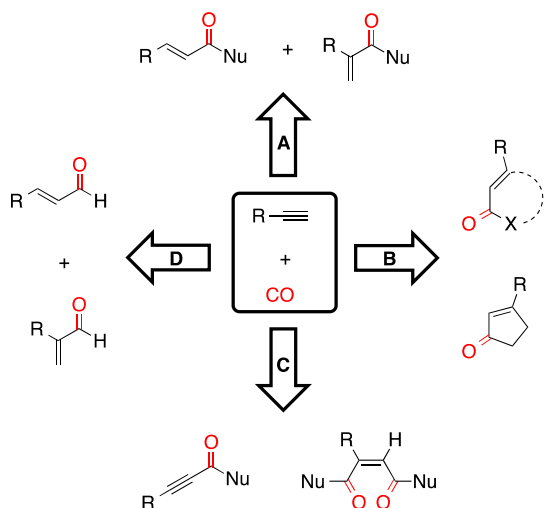
## Palladium-catalyzed carbonylation of alkynes

Among the different catalytically active metals for the carbonylation of alkynes, palladium displays very high activity and versatility. It has received considerable attention in recent years and it is even used to produce important industrial intermediates on large scale.<sup>3,10</sup> Several types of carbonylation reactions can be catalyzed by palladium and significant efforts have been made to control the regio- and stereoselectivity in these reactions. The intense research activities in this area are reflected in the number of reviews, which cover this topic in different ways.<sup>11–13</sup> Therefore, only the most important and recent achievements in the field of palladium-catalyzed carbonylations will be discussed. The chapter is subdivided according to the reaction type.

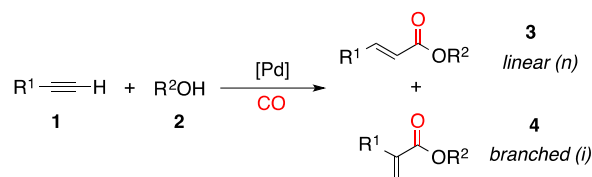
## Intermolecular alkoxy- and hydroxycarbonylation

The palladium-catalyzed carbonylation of alkynes with carbon monoxide and water is generally referred to as the hydroxycarbonylation reaction. When alcohols are used instead of water, the so-called hydroesterification or alkoxy-carbonylation of alkynes takes place. These reactions allow for the straightforward and atom-efficient preparation of  $\alpha,\beta$ -unsaturated acids and esters, respectively. In general, mixtures of linear and branched products are produced if terminal alkynes are employed (Scheme 1). The used catalyst, reaction conditions, and substrate can influence the regioselectivity.

The development of a versatile catalyst system based on palladium started with the early work of Tsuji and co-workers in 1966.<sup>14,15</sup> They published the palladium-catalyzed (Pd/C or PdCl<sub>2</sub>) carbonylation of propargyl alcohols and chlorides in methanol or benzene. Numerous further developments followed, where different catalysts were employed leading to product mixtures with a preference for branched  $\alpha,\beta$ -unsaturated esters **4**. One early example on the regioselective alkoxy-carbonylation is the work of El Ali and Alper, who employed Pd(OAc)<sub>2</sub> or Pd(dba)<sub>2</sub> in combination with the ligand dppb (**5**, dppb = 1,4-bis(di-phenylphosphino)butane) (Scheme 2).<sup>16</sup> The reactions were performed under harsh conditions (80 bar CO, 150–190 °C), affording the branched products with high selectivity (up to >99%), but only in moderate yields (25–60%).



**Figure 1.** Scope of alkyne carbonylations: (A) amino-, alkoxy-, hydroxy- and thiocarbonylations; (B) cyclocarbonylations; (C) oxidative carbonylations; (D) hydroformylations.



**Scheme 1.** Alkoxy- and hydroxycarbonylation of alkynes to regioisomeric products **3** and **4**.

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