Coordination Chemistry Reviews 293–294 (2015) 279–291

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

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

Transition metal complex catalyzed carboxylation reactions with CO_2

Dingyi Yu, Siew Ping Teong, Yugen Zhang*

Institute of Bioengineering and Nanotechnology, 31 Biopolis Way, The Nanos, #04-01, Singapore 138669, Singapore

ARTICLE INFO

Article history:
Received 30 June 2014
Received in revised form 29 August 2014
Accepted 1 September 2014
Available online 16 September 2014

Keywords:
Carbon dioxide utilization
Carboxylation
Transition metal catalyst

ABSTRACT

Transition metal complexes play a key role in catalytic carboxylation reactions with CO_2. Various metal complex catalytic systems have been developed for the carboxylation of different substrates that provide versatile methodologies for green organic synthesis. This review summarizes recent developments of CO_2 carboxylation reactions with C—C bond formation catalyzed by transition metal complexes. The contents in this review are arranged based on various transition metals and substrates of various functional groups. The reaction mechanisms and the role of metal catalysts will also be discussed.

1. Introduction

Carbon dioxide (CO_2) is a non-toxic, non-combustible and non-flammable gas. Carbon dioxide is the major source of greenhouse gas, hence it acts as an attractive C1 building block in organic synthesis since it is abundant, renewable and environment friendly [1,2]. Its utilization, as opposed to storage of CO_2, is indeed more attractive especially if its conversion to useful products is economical. Carboxylic acids are one of the most important types of compounds in medicinal chemistry and fine chemicals synthesis [3]. Although there are many well-established protocols for the preparation of carboxylic acids, the direct carboxylation of carbon nucleophiles using CO_2 as the electrophile is the most attractive and straightforward method [3]. The formation of a stable C—C bond typically facilitated by the insertion of CO_2 into a metal–carbon bond [3–5] is desired for CO_2 fixation. Recently, this protocol has been expanded to transition metal complexes catalyzed carboxylation of less reactive organometallic reagents where catalytic insertion of CO_2 into less polarized metal–carbon bonds with high chemoselectivity was achieved under mild reaction conditions [6–8]. Catalytic systems for the synthesis of carboxylic acids by direct CO_2 carboxylation without using stoichiometric organometallic reagents have also been developed [9]. Transition metals involved in the catalytic CO_2 carboxylation reactions mainly include coinage metals (Group 11, Cu, Ag and Au), iron group (Fe and Ni) and platinum group (Ru, Rh, Pd and Ir). This review will summarize recent developments of CO_2 carboxylation reactions with C—C bond formation catalyzed by transition metal complexes.

2. Carboxylation of organometallic reagents with CO_2

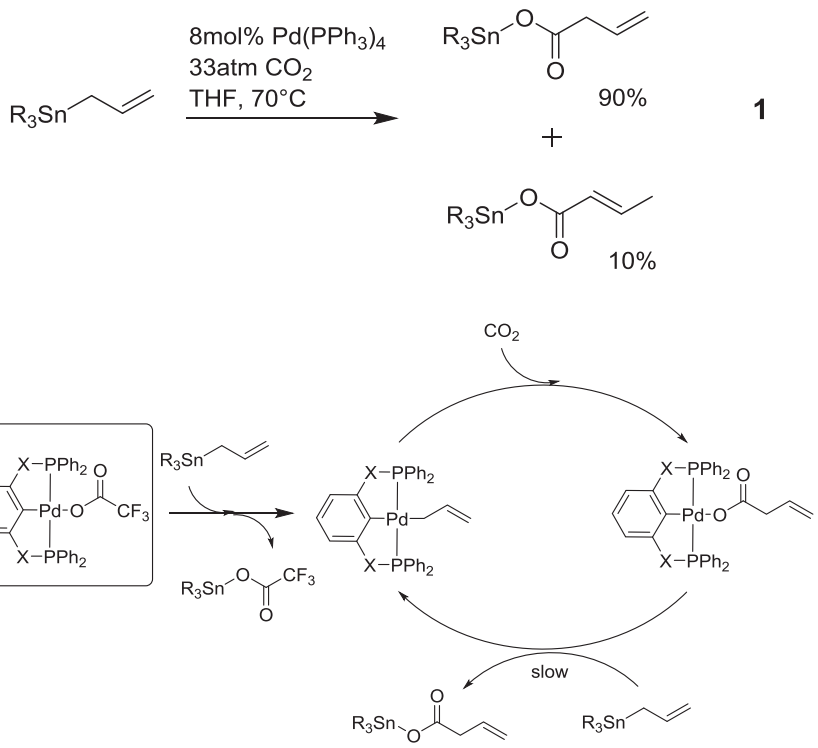
Direct carboxylation of organometallic reagents with CO_2 has been well-studied and applied in organic synthesis [3,4]. The advantages of this protocol include avoiding harsh reaction conditions and using CO_2 as a green and sustainable source. On the other hand, this synthesis needs a stoichiometric amount of expensive and sensitive organometallic reagents. Other than organolithium and organomagnesium reagents, organocopper [4] and organoaluminum [5] reagents have also been successfully transferred to carboxylic acids through CO_2 insertion. However, wide usage of these methods is limited by the synthesis of related organometallic reagents.

2.1. Ni- and Pd-catalyzed carboxylation of R—M (M = Sn, Zn) reagents with CO_2

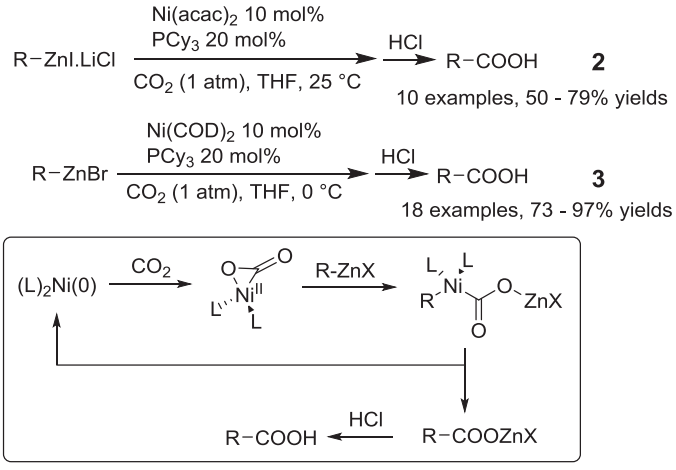
As organolithium and Grignard reagents are highly reactive, the substrates must not contain sensitive functional groups such as aldehydes, ketones or nitriles. Recently, alternative methods that can catalytically insert CO_2 into metal–carbon bonds with high chemoselectivity under mild reaction conditions have been developed. The first transition metal catalyzed CO_2 insertion into less polarized metal(tin)-carbon bonds to form carboxylic acids was reported in 1997 by the Nicholas group (Eq. 1) [6]. CO_2 insertion into allyl stannanes was catalyzed by palladium or platinum with phosphine ligands at high pressure (33 atm). Further developments were reported in 2006, where pincer-type palladium compounds

* Corresponding author. Tel.: +65 68247162.
E-mail address: ygzhang@ibn.a-star.edu.sg (Y. Zhang).

http://dx.doi.org/10.1016/j.ccr.2014.09.002
0010-8545/



Scheme 1. Wendt's pincer-type Pd ligand complex for carboxylation of allyl stannanes [7].



Scheme 2. Nickel(0)-catalyzed carboxylation of organozinc reagents [11].

were responsible for the high selectivity of the terminal alkene product (Scheme 1) [7]. Other types of palladium complexes have also been reported as catalysts in this reaction [10]. The reaction mechanism involved palladium transmetallation with allyl stannanes, followed by CO_2 insertion into Pd—C bond to form carboxylates.

Organozinc is another useful reagent for the transition metal catalyzed carboxylation reaction. Nickel–catalyzed coupling reactions of organozinc with CO_2 at room temperature have been reported [11], where Aresta's complex of $Ni(\eta^2\text{-}CO_2)(PCy_3)_2$ (Scheme 2) was a key intermediate. The phosphine ligands also played a significant role, where electron rich phosphines are essential for the oxidative addition of the metal to CO_2. Concurrently, the carboxylation of organozinc reagents with palladium and nickel catalysts under 0 °C in THF (Eq. 3) has been introduced [12]. The palladium catalysts gave higher yield for aryl-ZnBr while nickel catalyst works for both aromatic and alkyl organozinc reagents. Lithium chloride is essential for the carboxylation process, where a minimal yield of less than 5% was achieved without it. The reaction was applicable to secondary alkylzinc reagents and tolerant to a wide range of functionalities, which widens its opportunities for carboxylation. All of the reactions followed a similar mechanism consisting of oxidative addition of nickel (0) to CO_2, transmetallation with the organozinc reagent and reductive elimination to afford the corresponding zinc carboxylate (Scheme 2).

2.2. Cu-, Pd- and Rh-catalyzed carboxylation of R—B reagents with CO_2

Organocopper reagents are unique where the metal–carbon bond of moderate polarity, is ready for CO_2 insertion under ambient conditions and tolerant to most of the functional groups [13]. Copper catalysts can also catalyze various C—H and C-halogen activation reactions and many of them involve Cu—C bond intermediates [14]. These facts make copper catalysts a very promising choice for CO_2 transformation, especially with new C—C bond formation.

The research groups of Iwasawa [8,15] and Hou [16] developed transition metal catalyzed carboxylation of organoboronic esters with CO_2 under mild conditions. These new carboxylation reactions have regained considerable attention due to the widely used and highly convenient nucleophilic organoboronic ester reagents. The first report on a rhodium complex catalyzed carboxylation of organoboronic esters (Eq. 4) [15] revealed that the presence of CsF and dppe-type of ligands are critical to obtain the desired carboxylic acids in high yield. Soon after this development, Iwasawa [8] and Hou [16] independently introduced copper(I)-catalyzed carboxylation of aryl boronic esters (Eqs. 5 and 6). The copper catalyst systems possess obvious advantages over rhodium systems, as the copper catalyst is not only cheaper and more readily available, the broader substrate scope also allows for the synthesis of a wider range of functionalized carboxylic acids. The combination of CuI, bis-oxazoline ligand and excess amount of