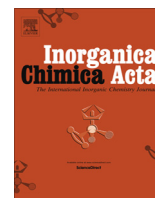




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Review

Recent improvements in the alkoxy carbonylation reaction catalyzed by transition metal complexes



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ABSTRACT

Palladium plays an almost exclusive role as catalyst in the alkoxy carbonylation of various substrates to produce esters or lactones, by incorporation of CO and a alcohol. The coordination sphere can be adapted by introduction of mono- or bidentate phosphorus-containing ligands, providing efficient tools to obtain with high turnovers, regio- and even enantioselectivities the incorporation of a COOR function onto a carbon atom. The use of CO, surrogates such as formates or even carbon dioxide are explored to operate this reaction. Adapted catalytic systems have been designed, sometimes with the assistance of microwave irradiation, to have an immobilization in Ionic Liquids, or $scCO_2$, or on various supports.

Even if less expensive metals than palladium are explored to provide comparable performances, green efficient tools are at the disposal of chemists leading to bulk and fine products as well.

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Philippe Kalck was graduated in chemistry from the Ecole Nationale Supérieure de Chimie de Toulouse (ENSCT) and the University Paul Sabatier in 1967. He remained in Toulouse for his doctoral research under the supervision of Professor René Poilblanc at the Laboratoire de Chimie de Coordination (LCC-CNRS), completing his Doctorat d'Etat in 1975. He combined research at LCC with teaching at the ENSCT until 1980, where he was appointed Professor at the Institut National Polytechnique de Toulouse (of which the ENSCT formed part) and funded a research group devoted to the catalysis of carbonylation reactions. This group has become the "Laboratoire de Catalyse et Chimie Fine" in the Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques Et Technologiques (ENSIACET), and since 2007 a team of 28 co-workers belonging to the LCC. He was particularly attached to promoting links between industry and fundamental research. He spent two years on secondment to Rhône-Poulenc Chimie between 1986 and 1988 to participate in the preparation of long-term research plans. His research interests include the design of highly selective catalysts and the molecular understanding of catalytic processes, fields in which he has published over 220 papers, filed 29 patents and supervised 55 PhD students. A part of his research activity is devoted to the preparation of heterogeneous catalysts by decomposition under mild conditions in a fluidized bed of coordination compounds. An application of these studies is the selective process for producing multiwalled carbon nanotubes. As Professor Emeritus since 2010, he is still active in coordination catalysis, especially to write book chapters and reviews.



Martine Urrutigoïty studied chemistry and biochemistry at the University Paul Sabatier of Toulouse, France and she received her PhD in biological organic chemistry. She joined in 1997 the research group "Catalysis and Fine chemistry" of Philippe Kalck and she first undertook her research on homogeneous catalysis on the carbonylation reactions including monoterpenes functionalization by asymmetric cyclocarbonylation. In 2009, she became full Professor at the National Polytechnic Institute of Toulouse (team "catalysis and fine chemistry of the Laboratoire de Chimie de Coordination). Now her main research includes enantioselective synthesis of intermediates, functionalization of natural products, by asymmetric carbonylation (alkoxy carbonylation and hydroformylation), cycloisomerization and hydrogenation reactions.

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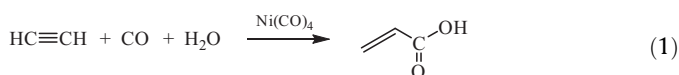
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0. Introduction

Late transition metal complexes allow transforming an unsaturated substrate by carbon monoxide embedding, so that functionalities can be produced which are of crucial interest in the fine chemistry. In the context of the sustainable development, the use of cheap and abundant building blocks for synthesizing value molecules represent an efficient way provided the catalyst precursor complex is efficient to give the only one expected product and to be fully recovered after catalysis. Since the pioneering work of the Reppe's research group at BASF on the carbonylation of acetylene in the presence of water to synthesize acrylic acid (Eq. (1)) with large amounts of $[\text{Ni}(\text{CO})_4]$ at 100 bar and 220–230 °C [1,2], many catalytic systems have been elaborated to transform an alkene or an alkyne into the corresponding acid or ester.



Thus, an unsaturated substrate gives rise to an acid or an ester with one more carbon atom. For instance, methyl acrylate can be prepared directly from acetylene, carbon monoxide and methanol at 30 bar and 160 °C starting from NiBr_2 , $[\text{Ph}_3\text{BuP}]\text{Br}$ and $[\text{BuPyridyl}]\text{Br}$ and the reaction can be easily extended to higher alcohols [3]. This reaction is no more operated on the industrial scale, and the carbonylation of propyne by the Shell process, involving a palladium acetate precursor, methyl di(2-pyridyl)phosphine in acidic medium, at 60 bar and 80 °C in the presence of methanol, with a 99.1% selectivity, has not been developed due to the high price of the alkyne [4]. A large part of the ca 3 million tons of global methyl acrylate production involves the methoxycarbonylation of ethylene to produce methyl propanoate, that is further reacted with formaldehyde to obtain with a 93% selectivity methyl methacrylate at a ca 40% lower cost than the classical hydrocyanation process of acetone [5,6].

The alkoxy carbonylation reaction, also called hydroesterification reaction, to produce esters has been covered by several relatively recent reviews, some of them focused on the mechanism of the methoxycarbonylation versus the CO/ethylene co-polymerization [7], on the asymmetric version [8–10], the various palladium complexes active in the carbonylation of alkene/alkyne substrates [11,12]. It appears attractive in this present contribution to emphasize the new trends published since 2006 and to focus on the improvements which have been elaborated to obtain efficient catalytic systems for reaching high atom-economy performances in this reaction. We analyze more especially the alkenes/alkynes, alkyl- and aryl halides starting substrates, new carbonylation

reactants such as CO_2 and formyl compounds and the emerging trends that appear in the literature.

1. Alkoxy carbonylation of alkenes and alkynes

Palladium complexes play a key-role in these carbonylation reactions affording the corresponding esters, because they work under mild conditions and allow for a broad substrate scope. A general didactic description has recently been published on the potential of this reaction [13,14]. In order to promote very selective reactions operating under stable conditions, it is crucial to determine which reaction parameters have a key role along the catalytic cycle. Since the initial works of Heck on palladium [15] and Knifton on platinum [16] mechanistic studies have been performed to highlight the main role of each parameter in the two catalytic cycles, which involve the more often proposed palladium-hydride pathway over the palladium-alkoxy carbonyl mechanism [17–21], sometimes transposed from studies in hydroxycarbonylation [22]. Moreover, recent kinetic investigations and theoretical calculations mainly confirm the formation, in the presence of acid promoters, of the palladium hydride active species either for alkenes [23,24] or for alkynes [25,26]. Along the catalytic cycle, the hydride transfer on one carbon atom of the coordinated alkene to palladium, to generate the alkyl species, is the discriminating step for the regioselectivity in the formation of the two linear/branched corresponding esters. The rate-determining step is the reaction of the alcohol onto the intermediate acyl species, generally called alcoholysis, providing the ester and restoring the active $[\text{Pd-H}]$ active species [23].

1.1. Intermolecular alkoxy carbonylation of an alkene

In many reports, the active species is generated in situ from a palladium salt (inter alia PdCl_2 , $\text{Pd}(\text{OAc})_2$, $\text{Pd}(\text{dba})_2$) a ligand and a promoter being either a Brønsted or a Lewis acid. Generally, for the carbonylation of a terminal alkene, addition to the palladium salt of a monophosphine ligand gives mainly rise to the branched isomer, whereas a diphosphine ligand significantly increases the linearity and in the case of very crowded ligands it is possible to reach 99.9%. In addition, the reaction parameters such as the CO pressure, the temperature, the presence of a peculiar solvent and an additive are adjusted in such a way that a high regioselectivity is obtained [11].

1.1.1. Carbonylation of alkenes

It has been found that trifluoromethane sulfonic acid is a good promoter to transform methyl pentenoate into dimethyladipate

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