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The series *Topics in Organometallic Chemistry* presents critical overviews of research results in organometallic chemistry. As our understanding of organometallic structure, properties and mechanisms increases, new ways are opened for the design of organometallic compounds and reactions tailored to the needs of such diverse areas as organic synthesis, medical research, biology and materials science. Thus the scope of coverage includes a broad range of topics of pure and applied organometallic chemistry, where new breakthroughs are being achieved that are of significance to a larger scientific audience.

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Carmen Claver

Editor

# Rhodium Catalysis

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# Preface

Rhodium coordination complexes or systems formed with rhodium in the presence of ligands, in particular phosphorus derivatives, have been extensively and successfully used as catalytic precursors in homogeneous catalysis for many years. The particular properties of both oxidation states of Rh(I) and Rh(III) allow for the successive oxidative addition, insertion, reductive elimination steps, and facilitate the activity and efficiency of the rhodium catalysts. The selectivity can be controlled and modified due to the versatility and modification possibilities of the ligands coordinated to the rhodium center. After the breakthrough of the application of  $\text{RhCl}(\text{PPh}_3)_3$  as a hydrogenation catalyst, rhodium catalysis blossomed enormously and cationic rhodium(I) phosphorus systems were also applied in hydrogenation reactions, being particularly attractive due to the use of chiral ligands allowing for the enantioselective hydrogenation reaction of prochiral substrates. The main characteristic of catalytic rhodium systems is the high selectivity and enantioselectivity achieved in most of the homogeneous catalytic processes. A relevant example is the hydroformylation reaction which involves a one-carbon chain elongation by the addition of carbon monoxide and hydrogen across a  $\text{C}=\text{C}$  double bond. It is well known that this is one of the main industrial processes carried out by homogeneous catalysis concerning the formation of aldehydes from alkenes. The use of the appropriate ligands allows the control of the regioselectivity and more recently the control of the enantioselectivity.

Many relevant books and reviews have been published about rhodium-catalyzed processes. This new volume “*Rhodium catalysis*” in the series “*Topics in Organometallic Chemistry*” intends to be an update of relevant, well-known reactions, as well as a summary of the lesser known applications of rhodium catalysis in organic transformations, together with topics related with sustainability. All the chapters are authored by research experts in each one of the topics presented.

It is shown in this volume how for hydrogenation reactions the monodentate ligands provide opportunities that would have been impossible to imagine with the bidentate ligands, owing to the possibility of producing complexes based on two different ligands. Rhodium-catalyzed C–H and C–X borylation is extensively reviewed in this volume. This area has received growing interest based on the

strong influence of rhodium to activate H–B and B–B bonds, the power of the ligands that modify the rhodium center to induce high levels of chemo-, regio-, and enantioselectivity, and the unrestricted mechanisms that can be deduced with the aid of density functional theory (DFT) calculations.

The impressive advances observed in recent years in the field of asymmetric hydroformylation are examined in this volume and conclude that the key to achieving high enantioselectivities is not the type of phosphorus function involved in the coordination to the metal, but rather the particular spatial arrangement of the coordinated ligand. Supramolecular strategies which have been very successful in asymmetric hydroformylation are also considered, indicating that the control of the second coordination sphere could be the key to achieving selectivity for the more challenging substrates.

Tandem reactions demonstrate how the efficiency of the reaction is improved when operating in the absence of isolating the intermediates, leading to the formation of more complex molecules in an economic manner. It is shown in this work how the rhodium-catalyzed tandem carbonylation reactions, involving the hydroformylation of an alkene followed by the transformation of the aldehyde product with a second reagent, can yield important chemicals for organic synthesis.

Other reactions are included in this volume, for example the rhodium-catalyzed decarbonylation developed over the last 50 years which has resulted in a wide range of reported catalyst systems and reaction protocols. The applications of these rhodium-catalyzed decarbonylation reactions are surveyed and discussed, including cross-coupling reactions, tandem reactions, and alternative methodologies for process intensification. The advances in rhodium-catalyzed cyclocarbonylation reactions are also discussed, including a variety of methods for the synthesis of carbo- and heterocyclic rings of different sizes, diastereoselective and asymmetric approaches, and the application of these reactions in the total synthesis of the important natural products (+)-asteriscanolide and (–)-ingenol. Rhodium catalysis for C–S bond formation is also considered. The recent developments in the reactions of cross-coupling, C–H activation, metathesis, thiolation, carbothiolation, and hydrothiolation for the C–S bond formation catalyzed by rhodium complexes, particularly highlighting the synthetic and mechanistic aspects, are summarized.

This volume also includes a chapter discussing the role of rhodium-based catalysts in homogenous and heterogeneous catalyzed CO<sub>2</sub> reductions, with well-described mechanisms.

This work presents the advances, new perspectives, and applications in a variety of representative rhodium-catalyzed reactions and will therefore be useful for researchers, graduate students, and synthetic chemists at all levels in academia and industry.

Tarragona, Spain

Carmen Claver

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