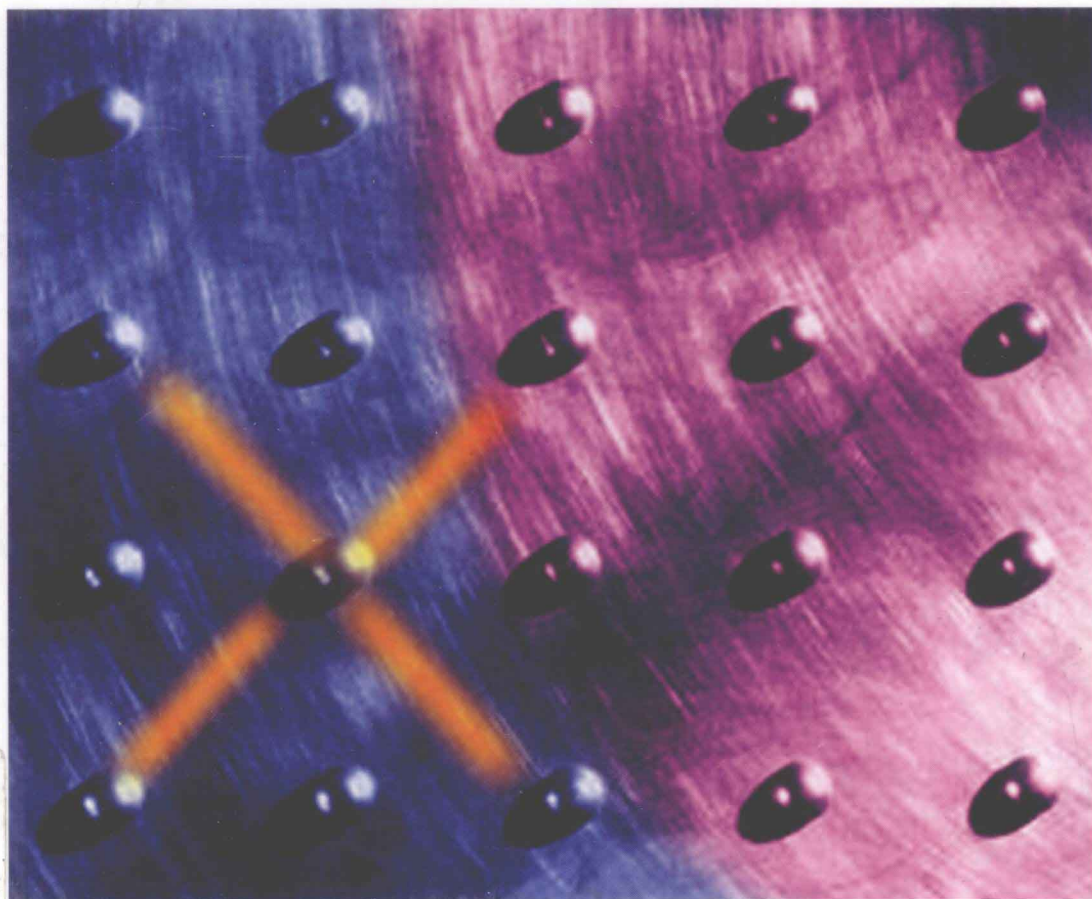


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Multimetallic Catalysts in Organic Synthesis



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Edited by

Masakatsu Shibasaki and Yoshinori Yamamoto



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Preface

Tyrosinase monooxygenases, which catalyze the ortho-hydroxylation of phenols, are dioxygen-activating enzymes. These proteins contain bimetallic centers, but it is not known in detail how the bimetallic centers are involved in enzyme activity, although there might be cooperative effects between the two metal atoms. Chemical transformations induced by bimetallic (or multimetallic) catalyst systems often have higher reaction rates and selectivities than those induced by monometallic and mononuclear complex catalysts, indicating that the development of multimetallic catalysts is one of the most important fields in chemical science for the 21st century.

A few years ago, Dr. Elke Maase suggested that we edit a book about multimetallic catalysts. Although we were very interested, there was some hesitation, since multimetallic catalysts were still very much under development. After several discussions, we decided to edit the book, because we believed that it would be very helpful to chemists who were interested in considering new ideas.

This book is about one of the major developments in current organic chemistry: the use and application of multimetallic catalysts for the synthesis of fine chemicals and structurally more complicated organic building blocks. Multimetallic catalysts have contributed tremendously to organic synthesis over the last few decades, and it seems clear that this trend will continue in future. The aim of this book is to provide readers with an interest in multimetallic chemistry for organic synthesis an insightful, up-to-date survey of this area. We have focused on the most important multimetal catalyzed methods as well as multitransition metal catalyzed reactions with a particular emphasis on the most recent developments. The literature available up to early 2003 was carefully reviewed, and, in some cases, important reactions that were published even in late 2003 were also incorporated. Due to space restrictions, we emphasized the methodology and paid less attention to the total synthesis of natural products compared to the synthesis of structurally less complicated building blocks and fine chemicals. We believe that in most cases the latter examples more clearly illustrate the principles that govern the reactivity of multimetallic catalysts in organic synthesis.

The book consists of three sections. The first describes efficient chemical transformations using two different metals such as the Nozaki-Hiyama-Kishi reaction, where two metals exist independently to effectively promote chemical transformations. The second section discusses asymmetric catalyses promoted by

heterobimetallic (or homobimetallic) catalysts, while the final section describes bimetallic (or multimetallic) catalyst-promoted transformations.

Finally, we sincerely hope that this book will be a valuable source of information for researchers working in academia and industry and that it will stimulate new development in this fascinating and intellectually appealing interdisciplinary area.

Masakatsu Shibasaki
Yoshinori Yamamoto

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1

Organic Synthesis with Bimetallic Systems*Shin Kamijo and Yoshinori Yamamoto***1.1****Introduction**

The application of bimetallic systems to organic synthesis has emerged dramatically in recent years, and great progress has been made in research aimed at developing reactions promoted with catalytic amounts of activating reagents. The cross-coupling reaction is a representative example of this type of transformation. In the early stages of the investigations, most studies were focused on transition metal (TM)-catalyzed reactions using main group organometallic compounds (R^2-M). The organometallic compound (R^2-M) was used as a coupling partner of the substrate (R^1-X); the cross-coupling reactions can be regarded as transformations promoted by a bimetallic system (*cat.* TM/*stoichiometric* R^2-M) (Figure 1.1a). Not only cross-coupling reactions (Section 1.2.1), but also reactions of π -allylpalladium complexes (Section 1.2.4) and nickel-catalyzed three-component coupling (TCC) reactions (Section 1.2.5) can be classified as belonging to category **a**. The conjugate addition of organomagnesium and -lithium reagents to Michael acceptors in the presence of catalytic amounts of copper salts also belongs to this category, but such organocopper reactions are not mentioned in this chapter since many excellent reviews and monographs have been published on these topics in recent years [1]. Another characteristic feature of these cross-coupling reactions is that an enhancement of the reaction rate is often observed in the presence of an additional metal salt (MX). The coupling reaction between R^1-X and R^2-M proceeds very smoothly in the presence of catalytic amounts of TM and stoichiometric amounts of MX (Figure 1.1b). Wacker reactions (Section 1.2.2), Heck reactions (Section 1.2.3), most of the reactions involving π -allylpalladium complexes (Section 1.2.4), and Nozaki-Hiyama-Kishi (NHK) reactions (Section 1.2.6) belong to this category **b**. We will discuss the reactions promoted by a combination of catalytic and stoichiometric amounts of metals (categories **a** and **b**) in the first section.

Recent studies have revealed that a wide variety of bimetallic catalytic systems composed of a transition metal and an additional metal salt (*cat.* TM/*cat.* MX) efficiently catalyze organic transformations, such as the cross-coupling reaction