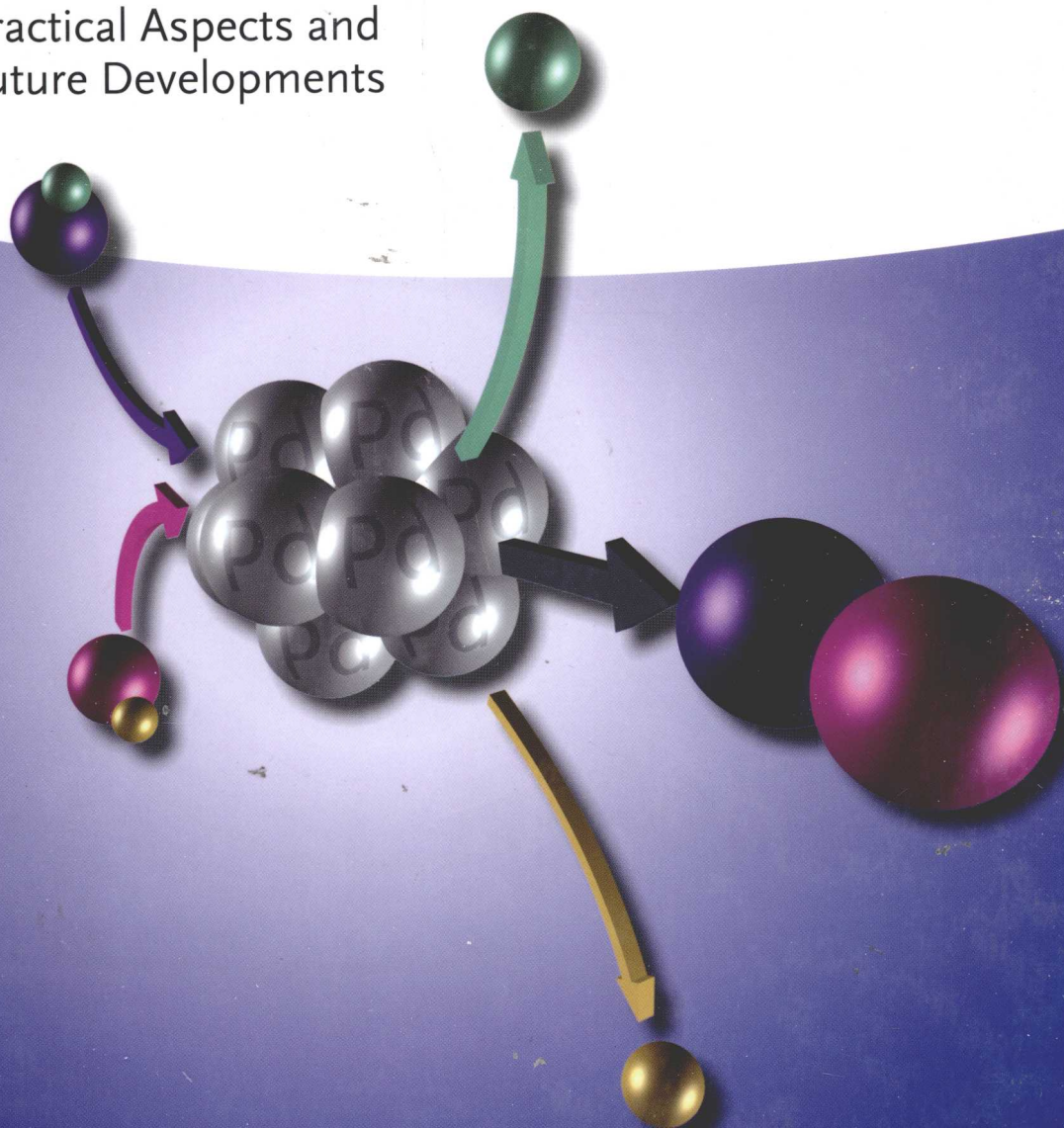


Edited by Árpád Molnár

Palladium-Catalyzed Coupling Reactions

Practical Aspects and
Future Developments



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Practical Aspects and Future Developments



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The Editor

Prof. Dr. Árpád Molnár

University of Szeged
Dept. of Organic Chemistry
Dom Ter 8
6720 Szeged
Ungarn

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Foreword

The field defined by the title of this monograph, “Palladium-Catalyzed Coupling Reactions,” has had a transformative effect upon organic synthesis, enabling bond constructions that could only have been dreamed about four decades ago. This has given rise to an immense and exponentially growing literature that encompasses far-reaching fundamental and applied topics. As of this writing, there is clearly “no end in sight” or approaching state of maturity.

The ongoing stream of developments can be ascribed to a number of factors, but one can begin with mechanism, where there are intricate subtleties regarding the homogeneous or heterogeneous nature of many transformations, as well as possibilities for cycles differing in the palladium redox states involved. Another driver would be applications, for example, the ability to effect new transformations or sequences of transformations, or render transformations that afford chiral products enantioselective or more highly enantioselective, or create catalysts with either improved functional group tolerance, or the ability to activate normally inert groups.

This line of thought leads into optimization issues. The desirability of longer lived catalysts capable of millions of turnovers is widely appreciated. One fundamental aspect of the quest for longer lived catalysts is to understand the processes by which they decompose or deactivate. When catalysts attain high turnover levels, recycling becomes especially attractive, and there are a plethora of strategies that can be applied, each with its own special strengths.

It is clearly a challenge to capture the essence of such a fast-moving field in a monograph. However, the Editor, Prof. Árpád Molnár, is superbly credentialed. He has many original research articles dealing with catalyst development to his credit, as well as authoritative reviews on the subjects of recyclable palladium catalysts and sustainable Heck chemistry. He has furthermore assembled an outstanding team of authors with many leading luminaries of the field. It is clear from the end product that this group has been up to the task, going beyond a mere collection of reports and giving readers new ways of thinking about palladium-catalyzed cross-coupling.

The leadoff chapter by Köhler, Wussow, and Wirth provides a textbook level introduction to various types of palladium-catalyzed cross-coupling reactions, representative types of molecular species that come into play, and equilibria involving monopalladium species, palladium cluster complexes, palladium nanoparticles, and bulk palladium. This is followed by Okumura’s treatment of high-

turnover zeolite-supported heterogeneous palladium catalysts, which illustrates the value of EXAFS and XANES techniques for catalyst characterization.

Recycling then becomes the focus in a chapter by Salih and Thiel, who describe the rapidly growing types of palladium catalysts that have been grafted to magnetic materials. The Editor, Molnár, then takes a turn, systematically reviewing the various classes of ordered porous solids that have been used as support materials for cross-coupling catalysts. Karimi, Abedi, and Zamani highlight a complementary theme, coupling reactions mediated by polymer-supported catalysts, in the following chapter.

The reaction medium then becomes the message. A chapter by Keßler, Scholten, Galbrecht, and Precht describes cross-coupling reactions in ionic liquids. Shaughnessy then plumbs the depths of coupling reactions in water. In both cases, volatile organic solvents are avoided. Catalysts with appropriate phase labels are generally required, but these provide “handles” for recovery. In the following chapter, Wang and Wang detail the intricacies of microwave-assisted coupling processes, in which greatly reduced reaction times can be achieved.

In an essential chapter, Molnár begins by describing key general issues in catalyst recovery, and then vividly conveys the state of the art, concluding with tabular summaries of numerous recycling studies. Subsequently, Huang and Wong analyze the nature of the true catalytic species in recipes employing heterogeneous palladium precatalysts. Much evidence supports a role for soluble “leached” moieties. Process then becomes the focus. Reynolds and Frost review coupling reactions that have been carried out using continuous-flow systems. The volume concludes with a survey of industrial applications of cross-coupling reactions by Dumrath, Lübke, and Beller.

In summary, this monograph informs, educates, and inspires. Both experienced practitioners and newcomers to this field will benefit from the insight and vision of a fantastic assembly of authors. Their superbly interwoven chapters are poised to influence every reader’s future, and foster the next generation of seminal developments in palladium-catalyzed cross-coupling reactions.

College Station, Texas

John A. Gladysz

November 2012

Preface

It all began in 1968 when Robert Heck published seven successive papers in the *Journal of the American Chemical Society*. In one of the articles [1], he reported the formation of styrene and *trans*-stilbene in the reaction of phenylmercuric acetate and ethene in the presence of stoichiometric amount of $\text{Li}_2[\text{PdCl}_4]$. He even put forward a correct mechanistic proposal and accounted for the stereochemistry of the reaction [2]. Further studies showed that palladium acetate can also act as catalyst and is capable of inducing the coupling of iodobenzene and styrene in the presence of stoichiometric amount of a base. Metallic palladium was subsequently shown to be active using the hindered tributylamine [3]. At about the same time, Mizoroki described the same coupling process performed under somewhat different conditions but could not pursue it further because of his untimely death [4,5].

Soon the field broadened and a range of related palladium-catalyzed carbon–carbon bond forming reactions were described in the 1970s followed by reports from the Suzuki and Negishi groups in the 1980s [6]. The chemical community, apparently, did not recognize the significance of these early observations. However, since the 1990s Pd-catalyzed coupling reactions have undergone a phenomenal development to encompass an amazingly rich and varied chemistry. Nowadays, these are indispensable and powerful methodologies for constructing diverse organic compounds including drugs, natural products, and new materials. The reactions may involve the use of phosphane and carbene ligands as well as palladacycles as catalyst precursors. General features are high activity and selectivity, tolerance of a wide range of functional groups, and mild conditions in most cases. In addition to C—C cross-couplings, efficient carbon–heteroatom couplings and, recently, functionalization with direct C—H bond cleavage have emerged as viable possibilities. In this still burgeoning field of organic synthesis, Pd stands out as the most prolific metal catalyst. The ultimate recognition of the seminal contribution by three pioneers of the field came in 2010 by awarding the Nobel Prize in Chemistry to Professors Heck, Suzuki, and Negishi.

This book is not about the chemistry of individual cross-coupling reactions. Rather, it is a collection of selected topics each discussing recent important achievements. Most subject areas covered in individual chapters have emerged and matured in recent years and appear to represent key issues for further successful development. Consequently, discussions will mainly center on recent progress over

the past decade. Each chapter concludes with a short discussion about potential for future advancements.

It has been a genuine enjoyment to be involved as Editor in this book project. It is my pleasure to warmly thank all the authors for their efforts in producing such an informed collection of contributions and sharing with the reader the latest news of their respective specialties. Twenty-three contributors from nine countries make this book an international achievement. Palladium chemistry, without doubt, has been a flourishing prime area of organic chemistry. It still is and we all believe that will certainly be. It is our sincere hope that our book will be of interest and use to those interested in this rich and fascinating field.

Finally, I am indebted to Dr. Elke Maase who initiated this book project in early 2011 for her encouragement to undertake this adventure and to Bernadette Gmeiner being a supportive project editor helping along the project.

Szeged

Árpád Molnár

September 2012

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List of Contributors

Sedigheh Abedi

Institute for Advanced Studies in
Basic Sciences (IASBS)
Department of Chemistry
Gava Zang
PO Box 45195-1159
Zanjan 45137-66731
Iran

Matthias Beller

Leibniz-Institut für Katalyse e.V. an
der Universität Rostock
Albert-Einstein-Str. 29a
18059 Rostock
Germany

Andreas Dumrath

Leibniz-Institut für Katalyse e.V. an
der Universität Rostock
Albert-Einstein-Str. 29a
18059 Rostock
Germany

Christopher G. Frost

University of Bath
Department of Chemistry and Centre
for Sustainable Chemical
Technologies
Claverton Down
Bath BA2 7AY
UK

Frank Galbrecht

Universität zu Köln
Institut für Anorganische Chemie
Greinstraße 6
50939 Köln
Germany

Lin Huang

Agency for Science, Technology
and Research
Institute of Chemical and
Engineering Sciences
1 Pesek Road, Jurong Island
Singapore 627833
Singapore

Babak Karimi

Institute for Advanced Studies in
Basic Sciences (IASBS)
Department of Chemistry
Gava Zang
PO Box 45195-1159
Zanjan 45137-66731
Iran

Michael T. Kefßler

Universität zu Köln
Institut für Anorganische Chemie
Greinstraße 6
50939 Köln
Germany

Klaus Köhler

Technische Universität München
Catalysis Research Center
Department of Chemistry
Lichtenbergstraße 4
85747 Garching
Germany

Christa Lübbe

Leibniz-Institut für Katalyse e.V. an
der Universität Rostock
Albert-Einstein-Str. 29a
18059 Rostock
Germany

Árpád Molnár

University of Szeged
Department of Organic Chemistry
Dóm tér 8
6720 Szeged
Hungary

Kazu Okumura

Tottori University
Department of Chemistry and
Biotechnology
Graduate School of Engineering
4-101, Koyama-cho Minami
Tottori 680-8552
Japan

Martin H.G. Prechtl

Universität zu Köln
Institut für Anorganische Chemie
Greinstraße 6
50939 Köln
Germany

William R. Reynolds

University of Bath
Department of Chemistry and Centre
for Sustainable Chemical
Technologies
Claverton Down
Bath BA2 7AY
UK

Kifah S.M. Salih

TU Kaiserslautern
Fachbereich Chemie
Erwin Schrödinger Straße 54
67705 Kaiserslautern
Germany

Jackson D. Scholten

Universidade Federal do Rio Grande
do Sul
Instituto da Química
Avenida Bento Gonçalves 9500
CEP 91501-970
Porto Alegre RS
Brazil

Kevin H. Shaughnessy

The University of Alabama
Department of Chemistry
Box 870336
Tuscaloosa, AL 35487-0336
USA

Werner R. Thiel

TU Kaiserslautern
Fachbereich Chemie
Erwin Schrödinger Straße 54
67663 Kaiserslautern
Germany

Jin-Xian Wang

Northwest Normal University
Department of Chemistry
Institute of Chemistry
An Ning Road (E.) 967
Lanzhou 730070
China

Ke-Hu Wang

Northwest Normal University
Department of Chemistry
Institute of Chemistry
An Ning Road (E.) 967
Lanzhou 730070
China

Andreas Sebastian Wirth

Technische Universität München
Catalysis Research Center
Department of Chemistry
Lichtenbergstraße 4
85747 Garching
Germany

Pui Kwan Wong

Agency for Science, Technology and
Research
Institute of Chemical and
Engineering Sciences
1 Pesek Road, Jurong Island
Singapore 627833
Singapore

Katharina Wussow

Technische Universität München
Catalysis Research Center
Department of Chemistry
Lichtenbergstraße 4
85747 Garching
Germany

Asghar Zamani

Institute for Advanced Studies in
Basic Sciences (IASBS)
Department of Chemistry
Gava Zang
PO Box 45195-1159
Zanjan 45137-66731
Iran

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