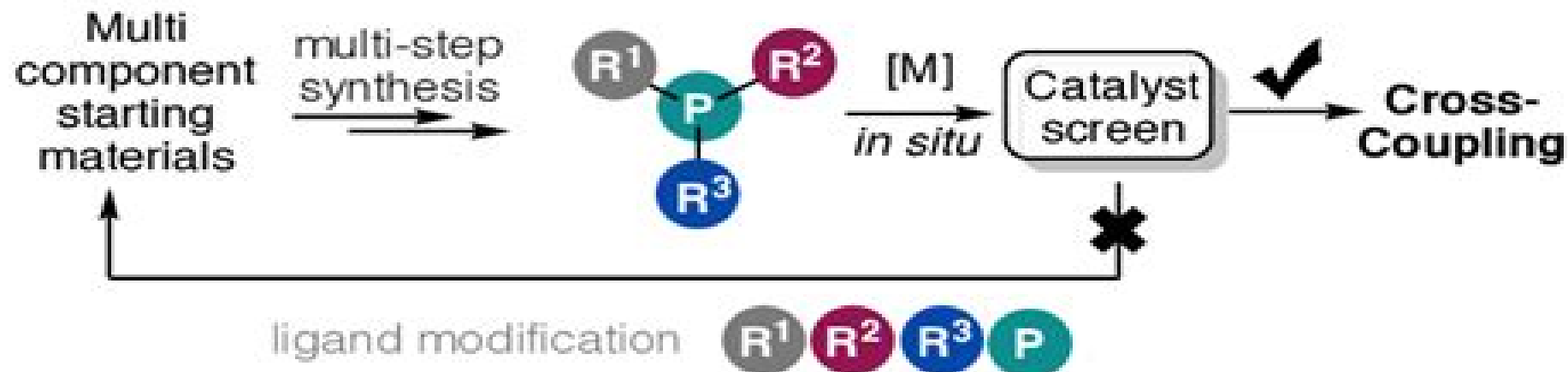


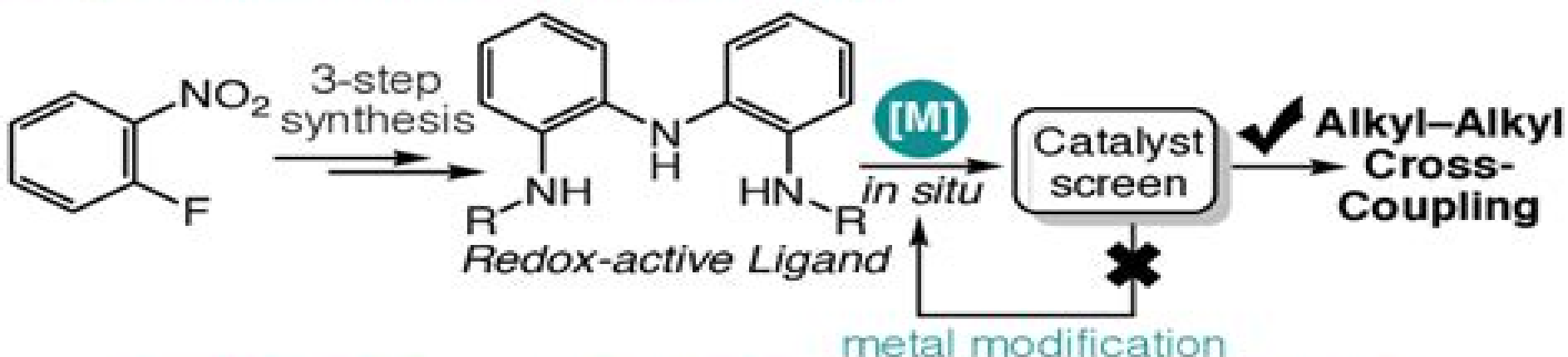
### a) Previous: Ligand Tuning

*multi-step synthesis of new ligand required between each catalytic screen*



### b) This work: Metal Tuning

*simple and efficient 1-step catalyst tuning*



Sc	Ti
Y	Zr
La	Hf

### This work: Early Transition Metal Cross-Coupling

- Redox-active ligand-based redox events
- Mechanism does not change between metals
- Metal tuning for optimization

# Metalcatalyzed Crobcoupling Reactions

**Armin de Meijere, Stefan Bräse, Martin  
Oestreich**



## **Metalcatalyzed Crobcoupling Reactions:**

*Metal-catalyzed Cross-coupling Reactions* François Diederich, Peter J. Stang, 2008-07-11 Carbon carbon bond forming reactions are arguably the most important processes in chemistry as they represent key steps in the building of complex molecules from simple precursors Among these reactions metal catalyzed cross coupling reactions are extensively employed in a wide range of areas of preparative organic chemistry ranging from the synthesis of complex natural products to supramolecular chemistry and materials science In this work a dozen internationally renowned experts and leaders in the field bring the reader up to date by documenting and critically analyzing current developments and uses of metal catalyzed cross coupling reactions A particularly attractive and useful feature that enhances the practical value of this monograph is the inclusion of key synthetic protocols in experimental format chosen for broad utility and application This practice oriented book can offer the practitioner short cuts to ensure they remain up to date with the latest developments **Transition**

**Metal-Catalyzed Couplings in Process Chemistry** Javier Magano, Joshua R. Dunetz, 2013-07-03 Transition metal catalyzed coupling reactions have a rich history that led to the awarding of the 2010 Nobel Prize in Chemistry to Professors Suzuki Heck and Negishi for their pioneering contributions to the field The coming of age of this active area of research is showcased in this book through case studies in which process chemists from the pharmaceutical industry share their personal experiences developing their own transition metal catalyzed couplings for the large scale manufacture of active pharmaceutical ingredients Authors from Pfizer Merck Boehringer Ingelheim Novartis Amgen GSK AstraZeneca and other companies describe the evolution of robust coupling processes from inception through early and late development including commercial routes where applicable This book covers a wide range of coupling transformations while capturing the lessons learned from each process Every case study details the optimization of at least one transition metal catalyzed coupling while elaborating on issues such as design of experiments scalability and throughput product purification process safety and waste management The important issue of metal removal and the different technologies available to accomplish this goal are also addressed Finally a section covers novel technologies for cross coupling with high potential for future applications on a large scale such as microwave and flow chemistry as well as green cross couplings performed in water With Forewords by Stephen L. Buchwald Massachusetts Institute of Technology Trevor Laird Editor of Organic Process Research and Development and Neal G. Anderson Anderson's Process Solutions LLC **Oxidative Cross-Coupling Reactions** Aiwen Lei, Wei Shi, Chao Liu, Wei Liu, Hua Zhang, Chuan He, 2016-08-17 The first handbook on this emerging field provides a comprehensive overview of transition metal catalyzed coupling reactions in the presence of an oxidant Following an introduction to the general concept and mechanism of this reaction class the team of authors presents chapters on C-C cross coupling reactions using organometallic partners C-Heteroatom bond forming reactions via oxidative couplings and C-H couplings via C-H activation The text also covers such groundbreaking topics as recent achievements in the fields of C-C and C-X bond formation

reactions as well as C H activation involving oxidative couplings With its novel and concise approach towards important building blocks in organic chemistry and its focus on synthetic applications this handbook is of great interest to all synthetic chemists in academia and industry alike Transition Metal Catalyzed Oxidative Cross-Coupling Reactions Aiwen Lei, 2018-12-14 This book is a comprehensive text covering the research and development trends in the booming field of transition metal catalyzed oxidative cross coupling reactions Oxidative cross coupling reaction is a new method to forming chemical bonds besides the traditional cross coupling reactions This book provides the answers to how this coupling reaction occurs and what its advantages are The palladium copper and iron catalyzed oxidative cross coupling reactions as the main focuses of interest are described in detail The oxidative cross coupling reactions catalyzed by other metals and transition metal free oxidative coupling reactions are also introduced This book provides a useful reference source for researchers and graduates in the field of transition metal catalyzed coupling reactions It is also valuable to researchers working in pharmaceutical companies fine organic chemical companies and etc Metal Catalyzed Cross-Coupling Reactions and More Armin de Meijere, Stefan Bräse, Martin Oestreich, 2013-12-04 This three volume book is the follow up handbook to the bestselling volume Metal Catalyzed Cross Coupling Reactions the definitive reference in the field In line with the enormous developments in this area this is not a new edition but rather a new book in three volumes with over 50% more content This new content includes C H activation shifting the focus away from typical cross coupling reactions while those topics and chapters found in de Meijere Diederich's book have been updated and expanded With its highly experienced editor team and the list of authors reading like an international Who's Who in the field this work will be of great interest to every synthetic chemist working in academia and industry **Cross-coupling Reactions** Joffrey Vrijdag, 2020 Cross Coupling Reactions An Overview opens with an overview of the fundamentals and applications of the young and fast developing area of transition metal catalyzed mediated oxidative dehydrogenative C H C H coupling reactions between two heteroarenes Continuing the authors highlight the recent advances regarding the ligand supported transition metal catalyzed domino cascade or one pot syntheses of various heterocycles involving cross coupling reactions The recent advances in Cu catalyzed tandem reactions for heterocycle synthesis are also addressed Cu metal chemistry has garnered attention as a potential alternative to precious transition metals being cheaper more sustainable and more easily available A comprehensive account of research on green chemical routes is provided involving various palladium metal based catalysts utilized in facilitating cross coupling reaction in aqueous media Reported decarboxylative cross coupling reactions are discussed along with suitable examples focusing on their mechanism of action **Applied Cross-Coupling Reactions** Yasushi Nishihara, 2012-12-14 Applied Cross Coupling Reactions provides students and teachers of advanced organic chemistry with an overview of the history mechanisms and applications of cross coupling reactions Since the discovery of the transition metal catalyzed cross coupling reactions in 1972 numerous synthetic uses and industrial applications have been developed The mechanistic studies of the cross coupling

reactions have disclosed that three fundamental reactions oxidative addition transmetalation and reductive elimination are involved in a catalytic cycle Cross coupling reactions have allowed us to produce a variety of compounds for industrial purposes such as natural products pharmaceuticals liquid crystals and conjugate polymers for use in electronic devices Indeed the Nobel Prize for Chemistry in 2010 was awarded for work on cross coupling reactions In this book the recent trends in cross coupling reactions are also introduced from the point of view of synthesis design and catalytic activities of transition metal catalysts

**Heterocycles from Double-Functionalized Arenes** Xiao-Feng Wu, Matthias Beller, 2015-02-02 The efficient synthesis of heterocycles has become one of the main branches in organic chemistry due to their use in the synthesis of natural products and pharmaceuticals Current sythentic strategies based on C H activation methodologies are met with many problems like harsh reaction conditions and low reaction efficiency Double functionalized chemicals offer a perfect alternative for the synthesis of heterocycles Heterocycles from Double Functionalized Arenes starts with a short discussion on the importance of heterocycles and a brief introduction on the preparation of double functionalized arenes Specific chapters then look at five membered heterocycles synthesis six membered heterocycles synthesis and macroheterocycles synthesis This is the first book dedicated to the topic of transition metal catalyzed coupling reactions of double functionalized arenes in heterocycle synthesis and can be used as a handbook for senior researchers and as an introduction for organic chemistry students

**Transition Metal Catalyzed Cross-Coupling Reactions** Ioannis D Kostas, 2021-12-23 Transition metal catalyzed cross coupling reactions have proved to be powerful tools for carbon carbon as well as carbon heteroatom bond formation in the development of synthetic methodologies for applications ranging from pharmaceuticals to materials This book consisting of an editorial two reviews and two articles focuses on recent promising research and novel trends in the field of cross coupling reactions employing a range of different catalysts A review by Kostas and Steele provides a survey of the research in the area of cross coupling catalytic reactions with transition metal complexes based on the thiosemicarbazone unit and a discussion of the prospects for future developments Another review by Polychronopoulou Shaya and co authors describes the progress made over the 21st century concerning the utilization of C sp<sup>3</sup> organoboranes as partners in metal catalyzed C sp<sup>3</sup> C sp<sup>2</sup> cross couplings such as B alkyl Suzuki Miyaura reactions The article by Waldvogel Breinbauer and co authors demonstrates for the first time the synthetic potential of combining the electro oxidative dehydrogenative cross coupling of ortho substituted phenols with Pd catalyzed cross coupling reactions In the second article St pni ka and co workers describe the preparation of palladium catalysts deposited over silica gel bearing composite amide donor functional moieties on the surface which were evaluated in the Sonogashira type cross coupling of acyl chlorides with terminal alkynes

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Mn Zn In Sn and Hg compounds These reactions provided an indispensable and simple methodology for preparative organic chemists Due to the simplicity and reliability in the carbon carbon carbon heteroatom and carbon metalloid bond formations as well as high efficiency of the catalytic process the reactions have been widely employed by organic chemists in various fields Application of the protocol ranges from various syntheses of complex natural products to the preparation of biologically relevant molecules including drugs and of super molecules and to functional materials The reactions on solid surfaces allow robot synthesis and combinatorial synthesis Now many organic chemists do not hesitate to use transition metal complexes for the transformation of organic molecules Indeed innumerable organic syntheses have been realized by the catalyzed reactions of transition metal complexes that are not achievable by traditional synthetic methods Among these the metal catalyzed cross coupling reactions have undoubtedly contributed greatly to the development of such a new area of metal catalyzed organic syntheses An excellent monograph for the cross coupling reactions and other metal catalyzed C C bond forming reactions recently appeared in *Metal catalyzed Cross coupling Reactions* Wiley VCH 1998

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Wiley VCH 1998      **Applications of Transition Metal Catalysis in Drug Discovery and Development** Matthew L. Crawley, Barry M. Trost, 2012-07-03 This book focuses on the drug discovery and development applications of transition metal catalyzed processes which can efficiently create preclinical and clinical drug candidates as well as marketed drugs The authors pay particular attention to the challenges of transitioning academically developed reactions into scalable industrial processes Additionally the book lays the groundwork for how continued development of transition metal catalyzed processes can deliver new drug candidates This work provides a unique perspective on the applications of transition metal catalysis in drug discovery and development it is a guide a historical prospective a practical compendium and a source of future direction for the field      Transition Metal-catalyzed Carbon-carbon Cross-coupling Reactions Using Sulfonyl Derivatives Srinivas Reddy Dubbaka, 2005      Transition-metal Catalyzed Cross-coupling Reactions Involving Inert C-Cl and C-H Bonds Zhiyong Hu, 2021      *C-C Cross Couplings with 3d Base Metal Catalysts* Xiao-Feng Wu, 2023-06-13 This volume presents recent progress on 3d base metal catalyzed C C cross coupling reactions The contributions provide detailed discussions on the use of cheap metal catalysts such as Cr Mn Fe Co Ni Cu and Zn to construct Csp<sup>2</sup>-Csp<sup>2</sup>, Csp<sup>2</sup>-Csp<sup>3</sup> and Csp<sup>3</sup>-Csp<sup>3</sup> bonds with a variety of substrates These non noble metal catalyst have many advantages such as being inexpensive having low toxicity and are environmentally benign Therefore the use of cheap metal catalysts in organic synthesis has gained much attention in efforts to develop more sustainable synthetic green chemistry Each chapter is written by international experts in the field and is a great resource for students researchers and chemists working in industry to gain an overview on the latest developments      **Transition Metal Catalyzed Cross Coupling Reactions of Functionalized Organometallic Reagents** Anne Eeg Jensen, 2001      *Advances in Organometallic Chemistry*, 2017-06-08 *Advances in Organometallic Chemistry* Volume 67 contains authoritative review articles of worldwide known researchers on the field of organometallic chemistry covering topics in organometallic synthesis reactions mechanisms homogeneous catalysis and more Updates in this new volume include chapters on Group 6 Metal Fischer Carbene Complexes Versatile Synthetic Building Blocks Recent Advances in Transition Metal Catalyzed Cross Coupling Reactions With Tosylhydrazones Oxidative Functionalization of Late Transition Metal Carbon Bond and Biaryl Synthesis via C H Bond Activation Strategies and Methods This book will benefit a wide range of researchers involved in organometallic chemistry including those working on synthetic protocols mechanistic studies and practical applications Contains contributions from leading authorities in the field of organometallic chemistry Covers topics in organometallic synthesis reactions mechanisms homogeneous catalysis and more Informs and updates readers on all the latest developments in the field Carefully edited to provide easy to read material

## The Enigmatic Realm of **Metalcatalyzed Crobcoupling Reactions**: Unleashing the Language is Inner Magic

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