

Editorial

Palladium Catalysts for Cross-Coupling Reaction

Kei Manabe

School of Pharmaceutical Sciences, University of Shizuoka, 52-1 Yada, Suruga-ku, Shizuoka 422-8526, Japan; E-Mail: manabe@u-shizuoka-ken.ac.jp; Tel.: +81-54-264-5754; Fax: +81-54-264-5586

Academic Editor: Keith Hohn

Received: 16 January 2015 / Accepted: 20 January 2015 / Published: 22 January 2015

Palladium-catalyzed cross-coupling reactions constitute one of the most important and useful transformations in transition metal-catalyzed reactions [1–3]. Although this research field emerged in the 1970s, it is still attracting considerable attention in synthetic and organometallic chemistry. New catalysts and catalytic systems are being developed to further expand the utility of the reactions. This Special Issue on “Palladium Catalysts for Cross-Coupling Reaction” covers the diverse aspects of the ever-evolving field of palladium catalysts in cross coupling chemistry.

This issue includes three reviews and three articles. The review by Ohashi and Ogoshi summarizes the recent development of palladium-catalyzed cross-coupling reactions of perfluoro organic compounds, such as tetrafluoroethylene and hexafluorobenzene [4]. One of the key steps of the reactions is the oxidative addition of a C–F bond to palladium(0). The finding that lithium iodide promotes the step, led the authors’ to develop efficient cross-coupling with organozinc reagents. The reactions with boronates are also presented. The review by Manabe and Yamaguchi covers the Pd-catalyzed cross-coupling reactions in which the site-selectivities between the two halo groups of dihaloarene substrates were controlled by the catalysts used [5]. Some new ligands for palladium were designed to realize high selectivity. This synthetic strategy is now a powerful tool for efficient synthesis of multi-substituted arenes. Obora and Ishii summarize recent progress in palladium-catalyzed oxidative amination of alkenes with amines, using O₂ as the terminal oxidant [6]. In this review, the uses of palladium catalysts combined with molybdovanadophosphate as a co-catalyst under O₂ are presented. In addition, the interesting results of amination using O₂ as the sole oxidant are also provided. In the article by Sajiki and Monguchi *et al.*, a successful example of continuous flow Suzuki–Miyaura coupling reactions of haloarenes with arylboronic acids is described [7]. Only 20 s were required for the single-pass flow through a cartridge filled with palladium on carbon to afford the desired coupling products in high yields. Takanami *et al.* developed a synthetic method of pentafluorophenyl- and related polyfluorophenyl-substituted porphyrins [8]. By choosing the appropriate palladium catalyst

and organozinc reagents, they obtained the desired porphyrins in excellent yields. Hikawa and Yokoyama *et al.* studied the palladium-catalyzed synthesis of bis(indolyl)methanes without protecting groups in water [9]. Their studies reveal the unique mechanism in which the (η^3 -benzyl)palladium system, generated from the palladium catalyst and benzyl alcohol, is involved.

In conclusion, these six papers clearly show the importance of palladium catalysts in cross-coupling chemistry and significantly contribute to further development in this field. I would like to thank all the authors of this Special Issue.

I am honored to be the Guest Editor of this Special Issue and would like to thank the reviewers for providing me with their valuable comments. I am also grateful to Keith Hohn, the Editor-in-Chief and all the staff of the *Catalysts* Editorial Office.

References

1. Negishi, E.-I. *Handbook of Organopalladium Chemistry for Organic Synthesis*; John Wiley & Sons Ltd.: New York, NY, USA, 2002.
2. Molnár, Á. *Palladium-Catalyzed Coupling Reactions*; Wiley-VCH: Weinheim, Germany, 2013.
3. De Meijere, A.; Stefan, B.; Oestreich, M. *Metal-Catalyzed Cross-Coupling Reactions and More*; Wiley-VCH: Weinheim, Germany, 2014.
4. Ohashi, M.; Ogoshi, S. Palladium-Catalyzed Cross-Coupling Reactions of Perfluoro Organic Compounds. *Catalysts* **2014**, *4*, 321–345.
5. Manabe, K.; Yamaguchi, M. Catalyst-Controlled Site-Selectivity Switching in Pd-Catalyzed Cross-Coupling of Dihaloarenes. *Catalysts* **2014**, *4*, 307–320.
6. Obora, Y.; Ishii, Y. Palladium-Catalyzed Intermolecular Oxidative Amination of Alkenes with Amines, Using Molecular Oxygen as Terminal Oxidant. *Catalysts* **2013**, *3*, 794–810.
7. Hattori, T.; Tsubone, A.; Sawama, Y.; Monguchi, Y.; Sajiki, H. Palladium on Carbon-Catalyzed Suzuki-Miyaura Coupling Reaction Using an Efficient and Continuous Flow System. *Catalysts* **2015**, *5*, 18–25.
8. Sugita, N.; Hayashi, S.; Ishii, S.; Takanami, T. Palladium-Catalyzed Polyfluorophenylation of Porphyrins with Bis(polyfluorophenyl)zinc Reagents. *Catalysts* **2013**, *3*, 839–852.
9. Hikawa, H.; Suzuki, H.; Yokoyama, Y.; Azumaya, I. Mechanistic Studies for Synthesis of Bis(indolyl)methanes: Pd-Catalyzed C–H Activation of Indole–Carboxylic Acids with Benzyl Alcohols in Water. *Catalysts* **2013**, *3*, 486–500.