

Editorial

Editorial *Catalysts*: Special Issue on Transition Metal Catalyzed Cross-Coupling Reactions

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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. Intensive research efforts continue to be made into finding ways of improving and expanding the scope of the processes, and the development of more efficient catalytic systems is a hot research topic of enormous academic and industrial interest. Improvements in catalyst design are continually being made and have led to the use of milder conditions, immobilisation on solid supports, biphasic systems for ease of separation, more benign solvents, etc. Research in this area has led to a wide variety of very efficient and useful procedures which are now most often known by the names of the scientists who pioneered their use, such as Suzuki–Miyaura, Mizoroki–Heck, Negishi, Sonogashira, Kumada–Tamao–Corriu, Migita–Kosugi–Stille, Tsuji–Trost, Buchwald–Hartwig [1–8]. These procedures are mainly based on palladium although other metals have been shown to be effective in a number of cases.

This Special Issue, consisting of 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 [9]. Phosphanes have traditionally been the ligands of choice for transition metal catalysis but, since they can often be water- and air-sensitive, a number of efforts have been made to develop water and air-tolerant phosphane-free ligands. Thiosemicarbazone ligands possessing a wide variety of coordination modes via N, S or additional donors are excellent candidates for catalysis under phosphane-free conditions, and their use in coupling reactions was first reported in 2004 and 2005 for the Heck and Suzuki reactions, respectively [10,11]. The fact that the ligands are relatively readily accessible and that the complexes formed show good stability make them popular subjects for investigation. This review covers a large number of thiosemicarbazone-based catalysts for a variety of cross-coupling reactions, indicating the importance of these systems in catalysis.

Another review by Polychronopoulou, Shaya and co-authors describes progress during the 21st century concerning the utilization of $C(sp^3)$ –organoboranes as partners in metal-catalyzed $C(sp^3)$ – $C(sp^2)$ cross-couplings, such as B–alkyl Suzuki–Miyaura reactions [12]. Important topics of this review include the use of organic halides or pseudohalides as coupling partners, the strong interest in C–O–alkyl electrophiles, and progress in the syntheses of stable and isolable sp^3 -boron reagents impacting the development of $C(sp^3)$ – $C(sp^2)$ cross-couplings.

The article by Waldvogel, Breinbauer and co-authors demonstrates for the first time the synthetic potential of combining the electrooxidative dehydrogenative cross-coupling of ortho-substituted phenols with Pd-catalyzed cross-coupling reactions [13]. This synthetic methodology resulted Bcl9 quateraryl α -helix mimetics for inhibition of protein–protein



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interactions (PPIs), and it is expected that it will find applications in the synthesis of oligoarene structures. In the first step of the process, two phenols undergo electrooxidative dehydrogenative cross-coupling for the formation of 4,4'-biphenols. For the next step, the researchers found it necessary to activate the phenols as nonaflates that could be conveniently subjected to Pd-catalyzed cross-coupling reactions, whereas triflates show considerable issues in the subsequent Pd-catalyzed reactions due to their hydrolytic lability against bases. The nonaflate moiety serves as a leaving group for iterative Pd-catalyzed Suzuki-cross-coupling reactions with substituted pyridine boronic acids.

In a second article, Štěpnička and co-workers describe the preparation of palladium catalysts deposited over silica gel bearing composite amide-donor functional moieties on the surface [14]. These heterogeneous catalysts were evaluated in the Sonogashira-type cross-coupling of acyl chlorides with terminal alkynes producing synthetically useful 1,3-disubstituted prop-2-yn-1-ones. In general, they showed a good catalytic activity under relatively mild reaction conditions even without addition of a copper co-catalyst, but a careful optimization was required as the catalytic properties are significantly affected by the reaction conditions (solvent and base) and depend on the nature of the functional pendant on the support's surface.

In summary, this collection of publications represents some of the progress and recent trends in the expanding field of transition metal catalyzed cross-coupling reactions. I wish to thank the authors of the publications for their valuable contributions, my colleague Dr. Barry R. Steele, and the editorial team of *Catalysts* for their kind support and fast response.

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