

Editorial

The genesis of cross-coupling reactions is often traced back to Ni-catalyzed reactions of Grignard reagents with aryl or vinyl halides reported in the 1970s. However, earlier reports by Kharasch in the 1940s already demonstrated the ability of simple iron salts to act as catalysts in couplings involving Grignard reagents. Unfortunately, these Fe and Ni-catalyzed processes were overshadowed by the meteoric development of palladium chemistry discovered shortly thereafter. Despite the undeniable maturity of Pd-based processes, the recent years have witnessed a renaissance in Fe and Ni-catalyzed reactions providing new dogmas for achieving practical and unconventional bond-disconnections that were beyond reach using classical Pd regimes. Consequently, cross-coupling reactions have impressively evolved from standard laboratory procedures into indispensable and routine techniques in chemical industry. As an illustrative example of the high value and tremendous impact of these chemical processes, the Nobel Prize in Chemistry 2010 was awarded jointly to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki for their important discoveries in palladium-catalyzed cross-coupling reactions.

Unlike palladium, iron and nickel can adopt a broad spectrum of oxidation states allowing thus different modes of reactivity and radical mechanisms. Likewise, the low-cost of nickel and environmentally-friendly character of iron make them privileged catalysts from the standpoints of economics and sustainability. This topical collection aims to cover recent developments in nickel and iron-based cross-couplings and illustrate how the intrinsic and unique properties of those first-row metals have enabled their use as convenient and highly versatile catalysts for a myriad of unprecedented, yet intriguing, chemical transformations. Accordingly, insightful contributions from several leading experts in this cutting-edge research field are collected, with particular emphasis on relevant recent progress and highlighting the utmost potential of both iron and nickel catalysis as broadly applicable synthetic tools in the realm of organic chemistry.

This topical collection begins with a set of contributions on Ni-catalyzed C–C couplings. Within this broad theme, N. Kambe focuses on reactions between alkyl electrophiles and organometallic reagents by means of Ni catalysis. G. Molander covers insightful discussion of photoredox/nickel dual catalysis using alkyl electrophiles. H. Gong describes Ni-catalyzed reductive coupling reactions between two distinct electrophiles. R. Martin comprehensively reviews the development of carboxylation events of unsaturated hydrocarbons with carbon dioxide. M. Tobisu and N. Chatani summarize key aspects on the use of phenol derivatives as versatile electrophiles via Ni-catalyzed C–O bond activation. The discussion on nickel catalysis is closed by a contribution of J. Yamaguchi and K. Itami on aromatic C–H functionalization processes including selected examples of natural product synthesis. This topical collection then shifts direction to discuss the use of environmentally-friendly and cost-efficient iron catalysis: L. Ackermann introduces most important results in Fe-catalyzed C–H functionalization processes, Z. Li gives a comprehensive understanding of cross-dehydrogenative couplings via iron catalysis, and J. Cossy closes the topical collection by covering Fe-catalyzed C–C coupling processes involving organometallic reagents. All in all, the reviews assembled herein provide an excellent overview of this burgeoning research area and will clearly open up new synthetic opportunities of paramount chemical significance. At present, however, limited knowledge has been gathered regarding the mechanism of some of the nickel and iron-catalyzed events disclosed herein, which sometimes are merely speculative and based on indirect experimental evidences. In this respect, mechanistic understanding of the underlying key elemental steps

through isolation of putative reaction intermediates will certainly fuel wider applications in the near future at the forefront of organonickel and organoiron chemistry.

I am grateful to Ruben Martin for kindly encouraging me to take on this task and deeply indebted to all distinguished colleagues who have contributed with their expert knowledge to make this comprehensive compilation on contemporary nickel and iron chemistry possible. Likewise, I would like to acknowledge the assistance of all the reviewers.

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