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Preface

Undoubtedly, most stoichiometric processes as well as elementary steps of relevance to catalytic cycles in organometallic chemistry involve two-electron changes in the metal configuration. However, one-electron processes are also of fundamental importance. They are associated to such basic phenomena as homolytic bond cleavage and atom transfer. They are of interest in core organometallic chemistry as well as at the interface with other disciplines, such as metal-mediated organic synthesis, polymer chemistry, electrochemistry, and biochemistry. The fundamental one-electron oxidative addition of alkyl halides, whereby a transition metal complex L_nM reacts with a R-X substrate to afford two new metals complexes, L_nM-R and L_nM-X , has been discovered over 50 years ago, but its relevance to the metal-catalyzed "atom transfer radical addition" (Kharash reaction) and to two different kinds of controlled radical polymerization process, namely by atom transfer and by reversible cleavage of the metal-carbon bond, have gained full appreciation only very recently. Other metal-mediated organic syntheses involving oneelectron changes are characterized by unusual selectivity. Electrochemically induced one-electron processes lead to enhanced reactivity, such as electron-transfer catalyzed ligand substitution, insertion, elimination, etc. Finally, one-electron processes involving transition metals are commonplace in bio-organometallic chemistry, the example of vitamin B-12 being perhaps the most widely appreciated.

The area of one-electron organometallic reactivity has grown spectacularly in recent years, following important advances in the fundamental understanding of the reactivity of open-shell organometallic compounds, in elegant applications to organic synthesis, and in the development of efficient metal-mediated radical polymerization techniques. For these reasons, the idea to collect recent contributions by specialists in this field in a special issue of the *Journal of Organometallic Chemistry* appeared timely. This area presents numerous opportunities for further development and applications. It is hoped that the results contained herein will stimulate further interest and contribute to open new research avenues.

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