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## Preface

For several decades, the development of selective, widely applicable methods for the functionalization of alkanes has remained one of the most alluring frontiers of homogeneous catalysis. The impetus for research in this area is to develop a means for the bulk utilization of saturated hydrocarbons, the world's most abundant organic resource, as a major chemical feed stock. Catalytic systems incorporating the C–H or C–C oxidative addition of alkanes by soluble transition metal complexes have come to be regarded as one of the most promising approaches to achieving this goal.

This line of research can be traced to Chatt and Davidson's observation in 1965 that the methyl C–H bonds of  $\text{Ru}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2$  undergo intermolecular oxidative addition to the ruthenium center. At that point-in-time, it had already been demonstrated that fine control of organic product selectivity could be achieved in transition metal complex based homogeneous catalytic reactions. Thus, it was quickly surmised that similar systems might be developed in which the intramolecular activation of aliphatic C–H bonds could initiate exotic catalytic sequences such as the selective functionalization of alkanes. Studies conducted during 1969–1971 by Shilov and co-workers provided the first demonstrations that a soluble platinum complex could catalyze the activation and functionalization of alkanes. Ten years later, the research groups of Crabtree and Felkin began to report the tantalizing results obtained from their studies of the catalytic dehydrogenation of alkanes by hydrido iridium and rhenium complexes. Further excitement was generated by the exquisite fundamental studies of alkane oxidative addition to  $\text{Cp}^*\text{ML}$  ( $\text{M} = \text{Ir}, \text{Rh}$ ;  $\text{L} = \text{PMe}_3, \text{CO}$ ) by research groups of Bergman, Graham, and Jones that began to be reported in 1982. Since that time an ever-growing number of researchers have engaged in an expanding scope of studies pertaining to the activation of

aliphatic C–H bonds by soluble transition metal complexes. Recently, it has been demonstrated that in addition to potential application to the production of bulk commodity chemicals, extremely useful methods for organic synthesis can be derived from catalytic systems for the selective activation of aliphatic C–H bonds. In parallel with the progress that has been made in the development of catalytic systems involving “C–H activation”, related homogeneous catalytic systems have been developed in which organic transformations are effected in reaction sequences involving the oxidative addition of strong C–C bonds.

In addition to the incentive provided by practical goals, researchers in this area are also attracted by the creative challenge of incorporating the ability of select types of transition metal complexes to activate aliphatic C–H and strong C–C bonds through oxidative addition into highly selective catalytic systems. Complexes must be designed and prepared that are reactive enough to overcome the inertness that is characteristic of these types of bonds yet constrained by relatively small energetic barriers in order to achieve high selectivity for the desired organic product. Furthermore, the complexes must be robust enough to withstand demanding reaction conditions such as elevated temperatures and/or low pH. The aspiration to create something that expresses such blend of power and finesse, charges research chemists in this area with a muse that is not unlike that of many fine artists and jazz musicians.

This special volume of the Journal of Molecular Catalysis: A, “Advances in the Development of Catalytic Systems Incorporating the Selective Activation of Aliphatic C–H and C–C Bonds by Transition Metal Complexes” presents accounts of the research that is currently being carried out by some of the leading investigators in this area. The collection of papers includes not only reports of recently discovered catalytic

systems, but also very insightful mechanistic studies of the fundamental process of the oxidative addition of  $sp^3$  C–H and strong C–C bonds at metal centers as well as computational studies of catalytic systems. While this volume is far from comprehensive in scope, I believe it will provide the reader with an exciting sampling of research that is currently underway.

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