Theoretical Aspects of Homogeneous Catalysis. Applications of *ab initio* Molecular Orbital Theory

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Kluwer Academic Publishers, Dordrecht, Boston, London, 1995
217 pages. £70
ISBN 0–7923–3107–9

This compact monograph commences with a brief introduction to quantum-mechanical organometallic chemistry which outlines the methods and strategies used in computational organometallic chemistry. There follows a discussion of the interpretation of the results of *ab initio* calculations. A brief bibliography for background reading is also provided.

Chapter 2 provides a substantial and excellent discussion of oxidative-addition reactions, by P.E.M. Siegbahn and M.R.A. Blomberg. The review focuses on the treatment of second-row complexes using *ab initio* methods. Geometry optimization of transition-metal compounds is discussed in detail. The results of calculations using several levels of treatment are considered; starting with a self-consistent field (SCF) approach, then using Møller–Plesset second-order perturbation theory (MP2) and at a higher level again the method of quadratic configuration interaction singles and doubles (QCISD).

The activation of H–H, C–H and C–C bonds is presented. It is concluded that the main state involved in the binding of insertion products for the second row is the S_0^1-state or the $D^{M+1}S_1$-state and at the transition state the S^0-state plays a key role. Consideration is also given to C–H activation in unsaturated hydrocarbons and to the activation of strained C–C bonds. The activation of methane by transition-metal cations is examined in considerable detail. This chapter provides an excellent survey of the state-of-the-art treatment of oxidative-addition processes by transition metals and serves as fine introduction.

Chapter 3, by N. Koga and K. Morokuma, deals with alkene migratory insertions and C–C bond formations. The *ab initio* RHF method has been used to study a variety of the alkene migratory insertions into an M–H bond. Berry pseudo-rotation (BPR) processes are considered in detail for the five-coordinate rhodium system $[Rh(H)(CO)_2(BH_3)C_2H_4]$, and for related systems. Other studies concern the possible reaction paths of hydrozirconation and acetylene insertion into the Sc–H bond of Cl_2ScH. Alkene migratory insertion–hydrogenation systems of rhodium are also explored in depth. Model systems relating to the role of the transition metal in the polymerization and tacticity of olefins are given a full analysis. This chapter comprises a clear review of the excellent recent work carried out by the authors.

Chapter 4, also by Koga and Morokuma, deals with carbonyl migratory insertions. Examples are chosen from early, middle and late transition-metal systems.

A density functional study on $[2_s+2_s]$ addition reactions in organometallic chemistry is given by E. Folga, T. Woo and T. Ziegler in Chapter 5, the focus being on $[2_s+2_s]$ reactions of industrial interest. Sigma-bond metathesis reactions involving biscyclopentadienyl scandium hydride and the analogous methyl derivative are discussed in detail. Studies related to the catalytic process of metathesis have been analysed and the decomposition pathway of metallocycles is presented.

Chapter 6, by A. Dedieu, is concerned with Wacker reactions. The *ab initio* theoretical studies are carried out on various steps of the Wacker process or related model reactions, and provide a rationalization of the activation of the coordinated olefin towards the incoming nucleophile (H_2O or OH^-). The studies show that a slippage of the coordinated olefin is central to the activation process and is induced by the incoming nucleophile.

The final chapter, by R. Zwaans, J.H. van Lenthe and D.H.W. den Boer, is concerned with a study of possible intermediates in the epoxidation of ethene catalysed by manganese(III)-chloroporphyrin. The calculations were performed using the restricted Hartree–Fock formalism incorporated in the quantum-chemical program system GAMESS-UK. The calculations provide insight into the oxidation mechanism.

Overall, this book provides a variety of excellent examples of the power of modern theory to investigate and to provide insight into the mechanisms of important reaction mechanisms of relatively complex molecular systems. It illustrates the strength of modern theoretical analysis to deal with real-world chemical reactions, and clearly confirms that the gap between theoreticians and experimentalists in this area is rapidly narrowing. I strongly recommend this book to those interested in understanding organometallic catalytic processes.

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