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Book review

Orbital Interactions in Chemistry; by T.A. Albright, J.K. Burdett and M.H. Whangbo. Published by John Wiley and Sons, New York 1985, £63.25. ISBN 0 471873934, 447 pages.

The simultaneous expansion of organotransition metal chemistry and ligand field theory during the nineteen fifties provided an excellent opportunity for collaborations between the leading experimentalists and theoreticians of the day. Unfortunately, the complexity of organometallic compounds prevented the formulation of completely reliable predictions, and the theoreticians had to resort to a mixture of rigorous symmetry arguments and semi-quantitative estimates of the interactions energies. At its most impressive this hybrid approach led to the successful prediction of cyclobutadiene complexes and the interpretation of hydride chemical shifts. On the other hand theoretical conclusions concerning the metal—carbon σ bond retarded the development of this area of chemistry. Uncertainties in the qualities of the theoretical predictions led to a fallow period during the nineteen sixties whilst chemists waited for computers capable of providing ab initio calculations, which would give reliable estimates not only of the geometries of complexes, but also their spectroscopic properties and reactivities.

It is ironical that when that time arrived, in the nineteen seventies, it was semi-empirical rather than ab initio calculations which have had the major impact on the thinking of organometallic chemists. The contributions of Roald Hoffmann and his coworkers have been particularly influential, because they directed the attention of synthetic chemists away from theoretically difficult questions, e.g. "Will this specific compound exist?" to more amenable geometric, conformational and reactivity problems.

"Orbital Interactions in Chemistry" gives an introduction to the semi-empirical molecular orbital calculations used widely by Hoffmann and his coworkers and many synthetic and structural chemists around the world. Its appearance is particularly timely not only because specialist organometallic journals are publishing an increasing number of theoretical papers, but also because the fragment and perturbation theory concepts underlying the approach are widely applicable and are becoming part of the common language of modern inorganic chemistry.

The book gives a very clear and well illustrated account of the basic concepts of molecular orbital theory and its application to simple Main Group molecules in the initial chapters. The effects of heterosubstituents and angular deformations on the geometries of molecules are developed using the concepts of perturbation theory and symmetry considerations. These principles are illustrated using examples from Main Group and polyene chemistry, and represent approximately half the book. The second half of the book deals with those aspects of bonding of greater interest to organometallic chemists. The material has been organised on the basis of geometrically related fragments. Therefore, following an introduction to octahedral, square-planar, tetrahedral and five-coordinate complexes, the bonding capabilities of ML_2, ML_3 and ML_4 fragments are developed. This organisation leads naturally to descriptions of the preferred conformations of metal-polyene complexes and their rotational barriers. Theoretical aspects of oxidative-addition, reductive-elimination and migration reactions are also discussed. The final chapters deal with the isolobal concept and the bonding in clusters.

The book has been illustrated consistently in the Hoffmann house style and the notation is uniform. Consequently, this is an attractive and easily assimilated book. It is ideally suited to a mature chemist wishing to come to terms with the current literature, but it is too long, detailed and specialised to be recommended as an introductory text for undergraduates and postgraduates. The price will also deter most students.

Although much in sympathy with the philosophy of the book and impressed by the professionalism of the presentation, it does in my view, have its blind spots, which will be apparent to chemists seeking a balanced introduction to theoretical organometallic chemistry. For example, thermodynamic aspects of metal—ligand bonds, the modification of metal reactivities by ligand electronic and steric effects, and important differences between metals in the same group of the Periodic Table are little discussed. These are the areas where the semi-empirical methods do not give a satisfactory account, and the general reader will have to look elsewhere for detailed discussions of such topics.

Inorganic Chemistry Laboratory, University of Oxford,
South Parks Road, Oxford OX1 3QR (Great Britain)

D.M.P. MINGOS