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Introduction

An introduction to this volume of *Journal of Organometallic Chemistry* devoted to theoretical methods must start with a reference to the Chatt–Dewar–Duncanson bonding model for ethene complexes. This symmetry-based model has proved to be so versatile and widely applicable that it has become an essential component of the way in which we teach the subject and even though it was proposed more than 40 years ago it remains the first line of thought when approaching a new bonding problem in organometallic chemistry. Sadly the completion of this volume has coincided with Professor Joseph Chatt's death in May 1994 and therefore I hope it will be viewed as a record of the way in which his important contribution has blossomed and tribute to his imagination, dedication and influence on organometallic chemistry.

Although the theoretical aspects of co-ordination chemistry were illuminated through the Crystal Field Theory in the 1950s and 1960s the detailed structural aspects of organometallic chemistry were not well understood until much later. During the 1970s semi-empirical molecular orbital calculations provided a new way of looking at geometric problems associated with organometallic compounds by underpinning symmetry and perturbation theory ideas. Although the limitations of the extended Huckel methodology are well documented it did enable chemists to trace the evolution of orbitals as the geometries of the complexes were changed. This approach was popularised by Hoffmann and his co-workers and widely applied to co-ordination and organometallic chemistry. The approach established that the bonding capabilities of metal fragments depended on the geometries of the ligands which made up the co-ordination environment. In addition it indicated that in non-centrosymmetric structures the metal d orbitals no longer retained their identities, but mixed extensively with the metal s and p orbitals which generated frontier orbitals which were critical for defining the bonding capabilities of the fragments. The knowledge of the bonding capabilities of these fragments when combined with simple perturbation theory ideas led to the *isolobal* analogy. The semi-empirical molecular orbital calculations also underpinned the Polyhedral Skeletal Electron Pair Theory, although once again criticisms were made concerning the inability of these types of calculations to accurately define the strength of metal–metal bonding in cluster compounds.

Despite these great insights into geometric problems which the semi-empirical molecular orbital calculations provided there were limitations which hampered its application to more detailed problems. For example, the fact that the calculations did not lead to mimima in the total energy, but a minimum in the sum of the one electron energies led to uncertainties in the accuracy of the predicted geometries. Similarly the extended Huckel method is notoriously bad at calculating the bond lengths in molecules. The great improvements in computing technology since the early 1970s had made it more and more practical to use more sophisticated calculations for geometric problems in organometallic chemistry. This volume summarises recent results using these more advanced methods and gives the non-specialist an insight into the current theoretical methodologies in organometallic chemistry.

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